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CHEMICAL DESULFURIZATION OF COAL: REPORT OF BENCH-SCALE DEVELOPMENTS

VOLUME I

TRW SYSTEMS GROUP

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Chemical Desulfurization of Coal: Report of Bench-Scale Developments

Volume 1

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The method used was the Meyer's process in which Pyritic sulfur is oxidized by ferric compounds to a water soluble form.

To produce a low sulfur coal to meet air quality standards.

15. Supplementary Notes

begin

16. Abstracts
Bench-scale and laboratory tests were conducted for chemical removal of sulfur (S) from coal. Approximately 100% of pyritic S was removed, using aqueous ferric salt solutions which, for the four coals tested, corresponded to an absolute removal of 1-3.5% by coal weight of S. The heat content of the coal increased and the ash content decreased as a result of pyrite removal. The pyritic S was removed from the coal as elemental S (40 mole %) and iron sulfate (60 mole %). Process operating temperatures of 50-130C, pressures of 1-10 atm, residence times of 1-16 hrs, and coal top sizes from 1/4-in. to 100 mesh were evaluated. Preliminary process design and cost estimation for a 100-ton/hr coal desulfurization plant indicated a cost of $2-3/ton of coal for removal of pyritic S from unwashed Appalachian or Eastern Interior Basin coals, depending on the amount of S removal required to produce a fuel which will comply with air quality regulations for fuel combustion and on any excess ferric ion consumption. Results of organic S removal tests indicate that additional studies are necessary before process feasibility can be assessed.

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Volume 1

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ABSTRACT

Bench-scale and laboratory testing for chemical removal of sulfur from coal was performed. Results for pyritic sulfur removal show approximately 100% removal of pyritic sulfur utilizing aqueous ferric solutions which, for the four coals investigated, corresponded to an absolute removal of 1-3.5% by coal weight of sulfur. In addition, the heat content of the coal increases and the ash content decreases as a result of removal of pyrite. The pyritic sulfur is removed from the coal as elemental sulfur (40 mole %) and iron sulfate (60 mole %). Process operating temperatures from 50°C to 130°C, pressures from 1 atm to 10 atm, residence times from 1 hr to 16 hrs, and coal top sizes from 1/4 in to 100 mesh were evaluated. Preliminary process design and cost estimation for a 100 ton/hour coal desulfurization plant indicated a cost of \$2-\$3/ton of coal for removal of pyritic sulfur from unwashed Appalachian or Eastern Interior Basin coals, depending both on the amount of sulfur removal required to produce a fuel product which will comply with air quality regulations for fuel combustion operations and on any excess ferric ion consumption.

Results from organic sulfur removal experimentation indicate that additional studies are necessary before process feasibility can be assessed.

This report was submitted in fulfillment of Modification 1 of Contract EHSD 71-7, under the sponsorship of the Office of Research and Monitoring, Environmental Protection Agency.

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1.0 CONCLUSIONS AND RECOMMENDATIONS

GENERAL CONCLUSIONS FOR PYRITIC SULFUR REMOVAL

1. The process for chemical removal of pyritic sulfur from coal (Meyers' Process) is capable of removing approximately 100% of the pyritic sulfur from cleaned or uncleaned coal.
2. All major process unit operations have been successfully demonstrated at the bench-scale.
3. The process may be designed in a variety of process flow schemes using state-of-the-art process equipment and construction materials.
4. Preliminary capital and operating cost estimates for a 100 ton/hour plant indicate an overall expense of \$2-\$3/ton to lower the sulfur level of applicable run-of-mine coals to a level which meets sulfur oxide emission regulations.
5. The Meyers' Process represents potentially major technology for the control of sulfur oxide emissions from combustion of coal in all coal combustion facilities (e.g., power plants, industrial boilers, etc.); this technology presently appears competitive with, and in some cases possibly more attractive than, flue gas scrubbing, coal gasification, coal deep cleaning, or coal liquefaction.

SPECIFIC CONCLUSIONS FOR PYRITIC SULFUR REMOVAL

1. Approximately 100% of the pyritic sulfur was removed by ferric ion multi-batch leaching from all four coals investigated: Lower Kittanning, Pittsburgh, Illinois No.5, and Illinois No.6 seam coals.
2. Extraction of 100 mesh top-size Lower Kittanning coal with 3 to 10 wt% (in ferric ion) ferric sulfate solutions (reagent grade or commercial) at ambient pressure and slurry reflux temperature (102°C) for 12 hours with continuous exchange of leach solution results in greater than 90% pyritic sulfur removal. Extrapolation of shorter extraction time data with Illinois No.5 coal indicates similar results.
3. Substantially reduced extraction times are indicated for equivalent pyritic sulfur removals at higher extraction temperatures (pressurized leaching); limited data indicates pyrite removals in excess of 80% during 2 to 4 hour extractions at 120°C to 130°C.
4. Ferric chloride solutions exhibit efficiencies similar to ferric sulfate solutions for pyrite removal from coal. Ferric sulfate is preferable because of its ease of removal from the treated coal and its reduced corrosion of process equipment.

5. Leaching temperature, leacher ferric ion to total iron ratio, coal particle top size, and pyrite concentration in coal were identified as the major parameters affecting pyritic sulfur leaching rate.

6. Leaching rate increases with increasing temperature, pyrite concentration and ferric ion to total iron ratio; it decreases with increasing coal particle top size.

7. The pyritic sulfur leaching rate is apparently inversely proportional to total iron concentration (expressed in wt%) when the latter exceeds 7 wt%. A direct dependence on total iron concentration may be present when the iron concentration drops below 4 wt%. Additional data beyond these values are required for precise determination of the total iron effect. It should be noted that total iron concentration influences the iron forms ratio, which has a strong influence on rate, and its effect on rate is therefore, difficult to separate.

8. Pyritic sulfur removal rates from Lower Kittanning coals extracted with ferric sulfate solutions of total iron concentration between 4 and 7 wt% are expressed by

   $r_L = K_L W_p^2 Y^2$ wt of pyrite removed/100 wts of coal/hour,

   where

   W_p = wt% percent pyrite in coal,

   Y = ferric ion to total iron weight ratio in leacher, and

   $K_L = A_L \exp(-E_L/RT)$, a function of temperature and coal particle size.

   This rate expression was fully validated for -100 mesh Lower Kittanning coal extracted with ferric sulfate solutions (4 to 7 wt% in iron) at 70°C to 102°C. It is also believed to be valid for Lower Kittanning coal up to at least -14 mesh, for similar top size Illinois No.5 coal, and for extraction temperatures in excess of 102°C.

9. Ferric ion oxidation of Lower Kittanning coal pyrite is totally selective; no measurable side reactions were observed. Illinois No.5 coal samples exhibited ferric ion comsumption in excess of that required for stoichiometric reaction with pyrite. It is believed that ferric ion reaction with the coal matrix took place but to an extent imperceptible from changes in heat content from determinations on fed and processed coal samples.

10. Pyrite from either coal reacts with ferric ion to yield sulfate and elemental sulfur at the approximate molar ratio of 1.5 to 1. This ratio of sulfur forms remains constant over a wide range of processing conditions.

11. The produced elemental sulfur is effectively recovered from the leached coal by extraction with toluene. The produced sulfate is readily recovered by three-stage washing of the leached coal with hot water.

12. Ferric ion regeneration obeys the expression

    $r_R = K_R [O_2][Fe^{+2}]^2$, moles of ferric ion regenerated per unit time,

    where

    $[O_2]$ = oxygen partial pressure in atmospheres,

    $[Fe^{+2}]$ = ferrous ion concentration in moles/liter, and

    $K_R = A_R \exp(-E_R/RT)$, a function of temperature only.

    The regeneration rate expression is valid for spent coal leaching reagent solutions of any total iron and ferrous ion concentration, for air or pure oxygen regeneration, and for at least the temperature range from 70°C to 120°C.

13. Spent reagent regeneration rates are more rapid than average leaching rates and are, therefore, more than adequate for continuous *ex situ* ferric ion regeneration. The exact regeneration time depends on the allowable ranges of ferrous ion concentration in the reactor; that is, on the concentrations of ferrous ion in the spent leach and regenerated solutions.

14. Process improvement experiments with -100 mesh Lower Kittanning coal indicated that simultaneous coal leaching reagent regeneration is probably the most efficient mode of process operation. Pyritic sulfur removal values in excess of 80% from a two hour extraction time were attained.

CONCLUSIONS FOR ORGANIC SULFUR REMOVAL

1. Of all the solvents studied p-cresol appears to be the most efficient solvent for organic sulfur extraction from coal.

2. Organic sulfur removal rates from Illinois No.5 and Lower Kittanning coals are influenced by temperature, organic sulfur concentration in the coal, coal particle size, and type of solvent used for extraction.

3. The organic sulfur extraction rate apparently increases with increasing extraction temperature and organic sulfur concentration in coal; the rate appears to decrease with increasing coal particle size (only -100 and -14 mesh coals were extracted).

4. Solvent retention on extracted coal depends on initial coal moisture content and coal drying conditions. The lowest solvent retention value attained was 2.6 wt% of processed coal which is an order of magnitude higher than desirable for economic p-cresol extractions.

5. Apparent organic sulfur removal values upon extraction with p-cresol for one hour at slurry reflux temperatures (∿200°C) ranged from 10 to 50 wt%. Low values (10% to 15%) were computed from data on recovered sulfur present in dissolved coal; high values (30% to 50%) were computed from total sulfur and sulfur forms analyses of starting and processed coal samples.

6. Exhaustive investigation of the accuracy of the analytical techniques used for sulfur determinations failed to identify the correct value of organic sulfur removal. Until the analytical problem is resolved, definite conclusions on process efficiency or feasibility can not be drawn.

RECOMMENDATIONS FOR PYRITIC SULFUR REMOVAL PROCESS DEVELOPMENT

1. The Meyers' Process should be tested at the pilot plant level. Only by pilot plant operation can integrated process feasibility and reliable process economics be established.
2. Bench-scale testing should be continued to support the pilot plant effort and to identify potential process improvements for subsequent evaluations.
3. Specific areas which should be evaluated initially at the bench-scale level include: simultaneous leach and regeneration modes; continuous process operation to obtain minor element system balances; techniques for increasing the leach and regeneration rates; and examination of reaction effects on the organic matrix leading to excess leach agent utilization.
4. A survey study should be performed to determine the widest applicability of the Meyers' Process for the desulfurization of United States coals.

RECOMMENDATIONS FOR ORGANIC SULFUR REMOVAL PROCESS DEVELOPMENT

1. A limited survey of the applicability of the process to United States' coals should be performed. This survey would indicate coals which may, because of their organic structure, be more susceptible to organic sulfur extraction than those coals previously tested.
2. A thorough examination should be made of analytical procedures for sulfur determinations in coals in order to provide an accurate assessment of the potential for extraction of organic sulfur from coal with p-cresol.
3. If the above work does not substantially demonstrate the potential of this approach to organic sulfur removal from coal, then development work on this technique should be suspended.

2.0 INTRODUCTION

National pollution abatement directions strongly suggest that it would be highly advantageous to have available a process which will inexpensively remove a major portion of the sulfur content of coal prior to combustion in order to comply with sulfur oxide emission levels governed by ambient air quality regulations and Federal Standards for Performance for New Stationary Sources. However, prior to this present investigation, the only advanced processes for the removal of the sulfur content of coal, other than coal gasification, were a) the physical separation type processes in which the high density of pyrite allows a physical separation of a coal fraction rich in pyrite from a coal fraction which is low in pyrite, and b) coal liquefaction processes, which dissolve the organic coal matrix leaving pyrites and other coal components in the residue.

Studies of the applicability of physical cleaning technology to the control of sulfur oxide pollution have shown that large coal losses are experienced in separating the quantities of pyrite required for meeting air quality regulations. Coal liquefaction processes will have high capital and operating expenses due to high pressure reactor costs, hydrogen consumption, and, with some processes, catalyst fouling and maintenance problems.

Because of the national need for additional technology to control sulfur oxide pollution from stationary sources, the personnel assigned to the TRW program for development of processes for the selective chemical extraction of sulfur from coal engaged in an intense effort to generate the data necessary for design of a pilot or demonstration unit based on the process for chemical removal of sulfur from coal (Meyers' Process).

This effort resulted in the attainment of the necessary data. In doing so, approximately 200 extractions and 50 leach solution regenerations, requiring approximately 4000 solution analyses and 2000 individual coal analyses, were performed.

The resulting report is necessarily quite large and, therefore, it is desirable at this point, to provide a guide to the reader who wishes to focus his attention on specific program results. The results are presented in three major sections:

- Selection of Coals for Evaluation,
- Pyritic Sulfur Removal, and
- Organic Sulfur Removal.

Those readers desiring to review the experimental data obtained for removal of pyritic sulfur from coal are directed to Sections 3.2.2.2 and 3.2.3.2 (pp. 23-31 and 48-71, respectively), as well as to the Appendix tables cited in these sections. Those readers desiring the engineering design and cost estimation information for the pyritic sulfur removal process are directed to Sections 3.2.4 and 3.2.5 (pp. 101-129), while those readers interested in ferric sulfate regeneration are directed to Sections 3.2.2.3, 3.2.3.2.3, and 3.2.3.3.8 (pp.32-37, 64-71, and 89-97, respectively) and to the cited Appendix sections. Concurrent leach and regeneration information is presented in Sections 3.2.2.4 and 3.2.3.3.9 (pp.38-39 and 97-100, respectively) and in the corresponding Appendix Sections.

3.0 PROGRAM RESULTS

3.1 Selection of Coals for Evaluation

Coals for study under this program from four coal beds, two each from the Appalachian and Eastern Interior Coal Basins, were jointly selected by the Environmental Protection Agency and TRW. These were (with specific counties):

- No.6, Randolf County, Illinois (Eastern Interior Basin)
- No.5, Fulton County, Illinois (Eastern Interior Basin)
- Pittsburgh, Greene County, Pennsylvania (Appalachian Basin)
- Lower Kittanning, Indiana County, Pennsylvania (Appalachian Basin)

These four coal beds were selected for evaluation because their distribution of sulfur forms is typical of coals east of the Mississippi River and because they represent major U.S. coal beds. The Pittsburgh bed has been described as the most valuable individual mineral deposit in the United States and perhaps in the world. Production of Pittsburgh seam coal has accounted for approximately 35% of the total cumulative production of Appalachian Basin bituminous coal up to 1 January 1965 and 21% of the total cumulative production of the United States to that date. The Lower Kittanning coal seam and its correlative beds contain even larger reserves than the Pittsburgh seam. The No.5 bed is the most widespread and commercially valuable coal bed in the Eastern Interior Coal Basin. The Herrin No.6 is second in commercial importance only to the No.5 bed.

All four coals were selected for laboratory-scale investigation, while one coal from each basin (Lower Kittanning and No.5) was selected for bench-scale emperimentation.

The U.S. Bureau of Mines supplied samples of the two Appalachian coals and the Illinois Geological Survey supplied the Eastern Interior Basin coals.

The dry analysis of each coal is presented in tabular form in Table 1. The sulfur forms, ash, and btu results are the average from analyses of at least three different samples. No significant difference between analyses of -14 and -100 mesh coals was found except that with 100 g samples the standard deviation was about twice as great for -14 compared to -100 mesh. The standard deviation given is for the -100 mesh coals.

The rank of each coal was detemined via ASTM Std.D388 (shown in Table 2). The fixed carbon, moisture, ash, sulfur, and btu content are used to calculate (according to the above ASTM method) dry, mineral matter free values for fixed carbon and volatile matter, and a moist mineral matter free value for btu. These values are used to rank coals.

Table 1. Program Coal Characterization

PITTSBURGH COAL
DRY ANALYSIS[a]

Proximate Analysis[a]	%
Ash	22.73 ± 0.48
Volatile	31.04
Fixed Carbon	46.23
btu	11,493 ± 60
Moisture[b]	2.80

Ultimate Analysis	%
Carbon	64.53
Hydrogen	4.26
Nitrogen	1.30
Chlorine	0.07
Sulfur	1.88
Ash	22.73
Oxygen (diff).	5.23

Sulfur Forms	%
Pyritic	1.20 ± 0.07
Sulfate	0.01 ± 0.01
Organic (diff).	0.68 ± 0.10
Total	1.88 ± 0.07

Rank Data

Dry Mineral Matter Free Basis	%
Fixed Carbon	61.34
Volatile Matter	38.66
btu (moist)	14,886
Rank-High Volatile A Bituminous Coal	

HERRIN NO.6 COAL
DRY ANALYSIS

Proximate Analysis	%
Ash	10.31 ± 0.28
Volatile	40.83
Fixed Carbon	48.86
btu	12,684 ± 55
Moisture[b]	7.4

Ultimate Analysis	%
Carbon	71.71
Hydrogen	4.94
Nitrogen	1.21
Chlorine	0.08
Sulfur	3.80
Ash	10.31
Oxygen (diff).	8.49

Sulfur Forms	%
Pyritic	1.65 ± 0.04
Sulfate	0.05 ± 0.01
Organic (diff).	2.10 ± 0.06
Total	3.80 ± 0.04

Rank Data

Dry Mineral Matter Free Basis	%
Fixed Carbon	55.77
Volatile Matter	44.23
btu (moist)	13,336
Rank-High Volatile B Bituminous Coal	

ILLINOIS No.5 COAL
DRY ANALYSIS[a]

Proximate Analysis	%
Ash	10.96 ± 0.26
Volatile	39.98
Fixed Carbon	49.06
btu	12,801 ± 58
Moisture[b]	10.20

Ultimate Analysis	%
Carbon	70.84
Hydrogen	4.95
Nitrogen	1.46
Chlorine	0.06
Sulfur	3.48
Ash	10.96
Oxygen (diff).	8.25

Sulfur Forms	%
Pyritic	1.57 ± 0.03
Sulfate	0.05 ± 0.01
Organic (diff).	1.86 ± 0.04
Total	3.48 ± 0.03

Rank Data

Dry Mineral Matter Free Basis	%
Fixed Carbon	56.15
Volatile Matter	43.85
btu (moist)	13,147
Rank-High Volatile B Bituminous Coal	

LOWER KITTANNING COAL
DRY ANALYSIS[a]

Proximate Analysis	%
Ash	20.77 ± 0.59
Volatile	20.69
Fixed Carbon	58.54
btu	12,140 ± 80
Moisture[b]	1.95

Ultimate Analysis	%
Carbon	68.26
Hydrogen	3.84
Nitrogen	1.20
Chlorine	0.08
Sulfur	4.29
Ash	20.77
Oxygen (diff).	1.56

Sulfur Forms	%
Pyritic	3.58 ± 0.08
Sulfate	0.04 ± .01
Organic (diff).	0.67 ± 0.10
Total	4.29 ± 0.06

Rank Data

Dry Mineral Matter Free Basis	%
Fixed Carbon	76.26
Volatile Matter	23.73
btu (moist)	15,524
Rank-Medium Volatile Bituminous Coal	

[a] All calculations done on a dry basis.

[b] Moisture before drying.

Table 2. Classification of Coals by Rank[a]*

Class	Group	Fixed Carbon Limits, percent (Dry, Mineral-Matter-Free Basis)		Volatile Matter Limits, percent (Dry, Mineral-Matter-Free Basis)		Calorific Value Limits, Btu per pound (Moist,[b] Mineral-Matter-Free Basis)		Agglomerating Character
		Equal or Greater Than	Less Than	Greater Than	Equal or Less Than	Equal or Greater Than	Less Than	
I. Anthracitic	1. Meta-anthracite	98	...	...	2	...	...	nonagglomerating
	2. Anthracite	92	98	2	8	...	...	
	3. Semianthracite[c]	86	92	8	14	...	...	
II. Bituminous	1. Low volatile bituminous coal	78	86	14	22	...	...	Commonly agglomerating[e]
	2. Medium volatile bituminous coal	69	78	22	31	...	...	
	3. High volatile *A* bituminous coal	...	69	31	...	14 000[d]	...	
	4. High volatile *B* bituminous coal	...	...	...	...	13 000[d]	14 000	
	5. High volatile *C* bituminous coal	...	...	...	...	11 500	13 000	
						10 500	11 500	agglomerating
III. Subbituminous	1. Subbituminous *A* coal	...	...	...	...	10 500	11 500	nonagglomerating
	2. Subbituminous *B* coal	...	...	...	...	9 500	10 500	
	3. Subbituminous *C* coal	...	...	...	...	8 300	9 500	
IV. Lignitic	1. Lignite *A*	...	...	...	...	6 300	8 300	
	2. Lignite *B*	...	...	...	...	...	6 300	

[a] This classification does not include a few coals, principally nonbanded varieties, which have unusual physical and chemical properties and which come within the limits of fixed carbon or calorific value of the high-volatile bituminous and subbituminous ranks. All of these coals either contain less than 48 percent dry, mineral-matter-free fixed carbon or have more than 15,500 moist, mineral-matter-free British thermal units per pound.

[b] Moist refers to coal containing its natural inherent moisture but not including visible water on the surface of the coal.

[c] If agglomerating, classify in low-volatile group of the bituminous class.

[d] Coals having 69 percent or more fixed carbon on the dry, mineral-matter-free basis shall be classified according to fixed carbon, regardless of calorific value.

[e] It is recognized that there may be nonagglomerating varieties in these groups of the bituminous class, and there are notable exceptions in high volatile *C* bituminous group.

*1971 Annual Book of ASTM Standards, pt. 19, ASTM, Phil., Pa. (1971), p 60

3.2 PYRITIC SULFUR REMOVAL

3.2.1 Process Concept

The concept of chemically removing pyrites from coal has not heretofore been thought practical as a solution to the sulfur oxide air pollution problem since it is known that iron pyrites are insoluble in any known liquids. For example, hydrochloric, hydrofluoric or sulfuric acid which dissolves many inorganic salts, has little of no effect on iron pyrites. On the other hand, it is well known that pyrites may be oxidatively converted to sulfates (soluble in strong acid) by an oxidizing agent such as nitric acid (1), hydrogen peroxide or chlorine (2). However, these oxidizing agents are not seriously advanced as the bases of processes for lowering the sulfur content of coal, since these reagents, which are strong enough to dissolve pyrite, also oxidize the coal matrix. Furthermore, nitric acid nitrates coal and chlorine greatly increases the chlorine content of coal (3). In addition, a number of groups (4,5) have investigated the use of hot alkali, but have now abandoned this approach presumably because much of the input base reacts with coal silicates, aluminates, and the organic matrix, causing excessive reagent and coal losses.

Aeration of coal in aqueous suspension has often been suggested for conversion of the pyritic sulfur content of coal to a soluble sulfate, as it is known that the mechanism of acid mine drainage involves slow conversion of pyrite to soluble sulfate. However, attempts to speed up this process under favorable conditions of air supply, temperature, and fineness of coal have only resulted in a reduction of residence time to weeks or months rather than years (4).

Thus, it was not thought possible to devise a practical process for chemically removing or dissolving the pyritic sulfur content of coal. It was therefore apparent that any economically viable process for the chemical removal of pyrite from coal would necessitate the utilization of an oxidizing agent (most likely aqueous) which a) is highly selective to pyrite, not significantly reacting with the organic portion of the coal matrix, b) is regenerable, c) is highly soluble in both oxidizing and reduced forms, d) is inexpensive and e) does not require high temperature or pressure for reaction with pyrite. It was discovered that aqueous ferric salts met the above combination of requirements, and these reagents form the basis for the Meyers' Process which is described below.

In the Meyers' Process aqueous ferric sulfate or chloride (mild but effective oxidizing agents) selectively oxidize the pyritic sulfur content of coal to form sulfate which dissolves into the aqueous solution and free sulfur. The free sulfur may than be removed from the coal matrix by steam or vacuum vaporization or solvent extraction and the oxidizing agent may be regenerated and recycled. It was not obvious at the start of our work that elemental sulfur could be removed from the coal matrix; earlier reports had indicated that coal heated with elemental sulfur resulted in recombination and liberation of hydrogen sulfide (6). The chemistry is outlined in eqs 1-4 below.

$$Fe_2(SO_4)_3 + FeS_2 \longrightarrow 3\ FeSO_4 + 2S \tag{1}$$

$$7Fe_2(SO_4)_3 + 8H_2O + FeS_2 \longrightarrow 15\ FeSO_4 + 8H_2SO_4 \tag{2}$$

$$S \cdot Coal \longrightarrow S + Coal \tag{3}$$

$$4FeSO_4 + 2H_2SO_4 + O_2 \longrightarrow 2\ Fe_2(SO_4)_3 + 2H_2O \tag{4}$$

The aqueous solution, which contains iron in both the ferrous and ferric state, may be regenerated in any number of ways, including air oxidation of the ferrous ion to ferric (eq 4). A fortunate aspect of this process lies in the fact that "iron is used to remove iron," so that on regeneration it is not necessary to separate the iron which is extracted from the coal from a metal oxidizing agent.

A block diagram of a process design which forms the basis for the current baseline flow system on the Meyers' Process is shown in Figure 1.

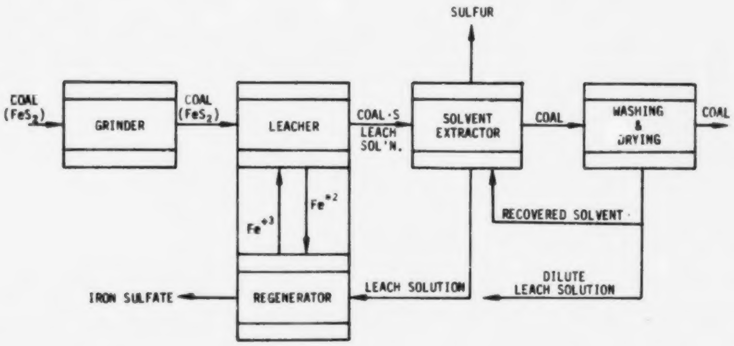

SULFUR
COAL (FeS_2)
GRINDER
COAL (FeS_2)
LEACHER
COAL·S
LEACH SOL'N.
SOLVENT EXTRACTOR
COAL
WASHING & DRYING
COAL
Fe^{+3}
Fe^{+2}
RECOVERED SOLVENT
IRON SULFATE
REGENERATOR
LEACH SOLUTION
DILUTE LEACH SOLUTION

Figure 1. Process Block Diagram

In this process scheme: (a) the coal is crushed to process size; (b) the coal is treated with aqueous ferric sulfate in a batch or continuous leaching unit; (c) depleted ferric sulfate solution is regenerated with oxygen, and excess iron sulfate (produced from coal pyrite) is removed; (d) elemental sulfur is removed by solvent extraction, and displaced aqueous solution is recycled; (e) residual iron sulfate and retained solvent are removed by washing and drying; and (f) desulfurized coal leaves the process unit.

3.2.2 Initial Laboratory Results

It was the objective of the initial laboratory effort to demonstrate the ability of ferric salts to remove maximum amounts of pyritic sulfur from the four coals under investigation, to demonstrate reagent regeneration both concurrent with, and separate from, the coal leach step, and to determine the gross effects of ferric salt anion variation, coal particle size and extraction conditions on the course of removal of pyritic sulfur. The initial laboratory results are described in the four sections which follow.

3.2.2.1 Reaction of Ferric Salts with Mineral Pyrite

The reaction of aqueous ferric salts with pyrite is a known reaction (7,8)but is not well detailed in the concentration ranges necessary for an economic process for removal of pyritic sulfur from coal. Therefore, the reaction was investigated in detail to provide the basic chemical data and laboratory and analytical experience needed for assessment of the Meyers' technique for removing pyritic sulfur from coal.

The reaction of ferric salt solutions with other sulfide minerals was also briefly studied in the hope that information could be obtained which could be utilized to improve the pyrite extraction rate or increase the elemental sulfur make. The oxidation-reduction reaction between ferric ion and iron pyrite is shown in eq 5.

$$FeS_2 + 2Fe^{+3} = 2S + 3\ Fe^{+2} \qquad (5)$$

The standard oxidation potential of the couple, $Fe^{+2} = Fe^{+3} + e^-$ in acidic solution is -0.77, while the standard oxidation potential of the persulfide ion, $S_2^{=} = 2S + 2e^-$ is ca. -0.1 in acidic solution. Thus, ferric ion is a strong enough oxidizing agent under standard conditions in acidic solution to oxidize the persulfide ion to free elemental sulfur. However, it should be borne in mind that the standard oxidation potentials are not necessarily directly applicable to the reaction of solid phases such as sulfur and pyrite.

The ferrous-ferric ion couple has an oxidation potential sufficiently negative to oxidize elemental sulfur to sulfurous acid since the couple $S + 3H_2O = H_2SO_3 + 4H^+ + 4e^-$ has a potential of -0.45; furthermore, the ferric ion can oxidize any sulfurous acid thus formed to sulfate as the couple $H_2SO_3 + H_2O = SO_4^{-2} + 2e^-$ has a potential of -0.20. Thus both sulfur and sulfate products can be obtained from the reaction between ferric salts and iron pyrite, as was indeed found to be the case during the experimentation reported below. It should be further noted that the formal oxidation potentials are highly variable according to the concentrations of the following ions: H^+, Fe^{+3}, Fe^{+2}, and anions; thus, the standard oxidation potentials are only indicative and not absolute. In addition, the overall ionic strength of the solution as well as the system temperature can significantly alter the effective oxidation potential.

The pyrite mineral material used for the planned experimentation was assessed for particle size distribution. Two photomicrographs (225X and 500X) are shown in Figures 2 and 3 . They show that there is a wide variation in particle size and that the particles are quite irregular. The photomicrographs were supplemented by sieve analysis (Table 3) using 200 (74μ), 325 (44μ), and 400 (37μ) mesh screens. It should be noted that 77% of the pyrite is >37μ in diameter, while the finely divided pyrite crystals in cleaned coal typically are found in clusters 2 to 20 microns in diameter.

Table 3. Sieve Analysis of -200 Mesh Pyrite

Sieve	Sieve Opening	% Passing Sieve
200	74	100
325	44	55
400	37	23

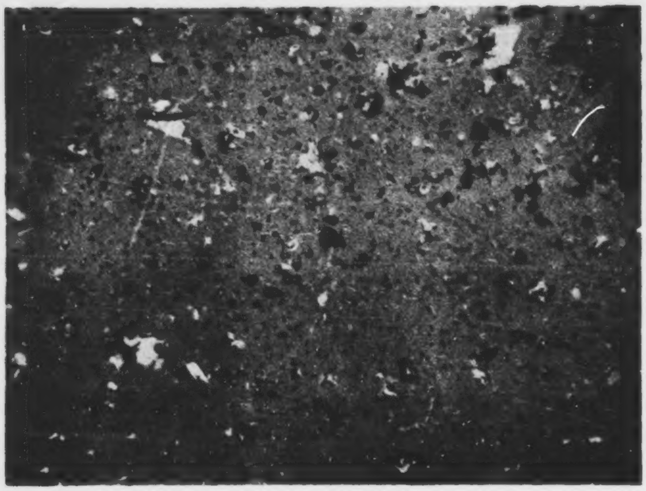


FIGURE 2. Photomicrograph of -200 Mesh Iron Pyrite Magnified 225X

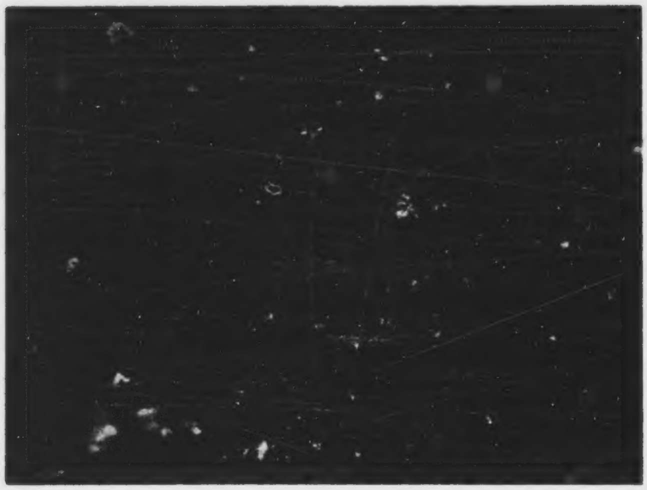


FIGURE 3. Photomicrograph of -200 Mesh Iron Pyrite Magnified 500X

The effects on mineral pyrite dissolution of extraction time, iron concentration, iron forms, added solvents, concurrent steam distillation, and anion variation are presented in Table 4. These extractions were performed in a sealed glass apparatus at atmospheric pressure, with stirring by a magnetic stirring bar. The sulfur formed was isolated by organic solvent extraction of the reaction mixture.

The effect of retention time (under conditions of constantly increasing ferrous ion concentration) is shown in Runs 1-5 (Table 4), where 96% removal is obtained in 8 hours. The effect of the starting ferric ion concentration (Runs 6-8) was extended to include concentrations to 3.6M (Runs 13, 14 and 16). Due to sulfate formation all the ferric ion is consumed during the 0.15M and 0.30M reactions. However, runs made with concentrations of 0.6M and higher show a leveling out in the extent of solution from 51% with 0.6M $FeCl_3$ to 62-64% at the higher (1.2, 3.6) molarities. This implies that the rate of reaction is controlled by diffusion of the reactant toward and products away from the surface of the pyrite. Run 15 was inadvertently treated with leach solution about 0.2M in ferrous ion. The presence of ferrous ion decreased the degree of extraction. The $SO_4^=/S$ ratios do not change and average 2.4 ± 0.4. The differences probably are not significant because they appear to be random.

The effect of acid concentration when 0.3M $FeCl_3$ is used is shown by Runs 7, 9 and 10 where the added acid concentration is varied up to 4.0M. Decreased conversion is noted at 4.0M relative to 0.0M and 1.0M while the sulfate to sulfur ratio decreases from 2.3 to 0.9. In a second set of experiments, Runs 14, 17 and 18 with 1-1.2M $FeCl_3$, HCl molarities of 0.0, 0.25 and 0.50 were studied. The resultant $SO_4^=/S$ ratio decreased slightly from 3.0 to 2.4 with the increase in HCl concentration while the degree of pyrite conversion dropped from 64% to 44%. Since $FeCl_3$ should form increasing amounts of the complex ion $FeCl_4^-$ to some extent with increasing HCl concentration, this reduced conversion is consistent with that observed for other complex ion reactants as reported below.

Since the most desirable sulfur byproduct formed from the process for removing pyrite from coal is elemental sulfur, three additional methods of reducing sulfate formation were investigated. Steam distillation of the sulfur from the reaction mixture and extraction of the sulfur into a solvent

Table 4. Extraction of Iron Pyrite (FeS_2) with Aqueous Ferric Chloride ($FeCl_3$) at 100°C.

Extraction Conditions										Extraction Data								Data Reduction				
						Ferric Chloride Leach Solution				Sulfur Balance			Residue after Extraction		Ferric Chloride Leach Solution After Reaction							
Expt No	Pyrite[a] wt	Pyrite Fe	Pyrite S	$FeCl_3$ Conc	HCl Conc	Fe^{+2}	Fe^{+3}	Total Fe	Reaction Time	S as FeS_2	S Free Elemental	S as Sulfate	Fe_2O_3	FeS_2	Fe^{+2}	Fe^{+3}	Total Fe	% Extraction of Pyrite	S Recovered All Forms	$SO_4^=/S$ ratio	Fe Recovered[c] All Forms	$\frac{Fe^{++}(\text{actual})^e}{Fe^{++}(\text{calc.})^d}$
	g	mM	mM	$\underline{M}$, V (l)	$\underline{M}$	mM	mM	mM	hrs	mM	mM	mM	mM	mM	mM	mM	mM		%		%	
1	2.25	16.9	33.8	0.5,1	0.1	7.7	447	454.7	2.0	17.3	2.2	8.8	---	8.7	72.3	394.5	466.8	49	84.0	3.2	101	1.27
2	2.25	16.9	33.8	0.5,1	0.1	7.7	447	454.7	8.0	1.3	6.4	20.5	2.6	0.7	173.5	276	449.5	96	83.4	2.9	95.8	1.16
3	2.25	16.9	33.8	0.5,1	0.1	7.7	447	454.7	16.0	0.2	[illegible]	21.0	5.1	0.08	177	278	455	99.5	85.5	2.5	97.7	1.12
4	2.25	16.9	33.8	0.5,1	0.1	7.7	447	454.7	24.0		3.5	21.2	8.4	0.0	193	268	461	100	88.1	2.3	99.4	1.20
5[b]	2.25	16.9	33.8	0.5,1	0.1	7.7	447	454.7	2.0	12.1	6.2	13.7	0.3	6.0	113	354	467	65	94.1	1.9	100	1.12
6	2.0	15.0	30.0	0.15,0.2	0.0	0.4	26.2	26.6	6.0	22.4	1.5	[illegible]	0.2	11.2	31.1	0	31.2	22.6	97.7	2.3	103	1.02
7	2.0	15.0	30.0	0.30,0.2	0.0	0.6	54.2	54.8	6.0	18.0	3.0	8.6	0.0	9.0	57.4	1.8	59.2	36.1	98.3	2.3	97.4	1.01
8	2.0	15.0	30.0	0.60,0.2	0.0	1.2	109.5	110.7	6.0	12.8	4.0	9.6	0.2	6.4	69.5	23.0	92.5	51.3	88.0	2.0	79.4	1.06
9	2.0	15.0	30.0	0.3,0.2	1.0	0.1	56.1	56.2	6.0	18.0	3.5	5.7	0.0	9.0	38.1	8.1	46.2	36.0	90.4	1.1	77.4	.89
10	2.0	15.0	30.0	0.3,0.2	4.0	0.1	57.4	57.5	6.0	21.3	2.8	4.1	0.0	10.7	27.0	34.8	61.8	25.9	94.0	0.86	99.9	1.22

[a] Pyrite mineral pulverized to -200 mesh, analyzed 89.8% as . The balance is silica with trace amounts of Zn, and Cu, 1.7 mM HCl soluble sulfate in untreated standard 2.00 g pyrite sample.

[b] 200 ml tetrachloroethylene added to leach solution.

[c] FeS_2, Fe_2O_3, Fe^{+3}, Fe^{+2}.

[d] Calculated on the basis of sulfur and sulfate produced.

[e] Based on Fe^{++} analysis.

Table 4, Cont'd. Extraction of Iron Pyrite (FeS_2) with Aqueous Ferric Chloride ($FeCl_3$) at 100°C (Continued)

Extraction Conditions										Extraction Data								Data Reduction				
		Pyrite				Ferric Chloride Leach Solution					Sulfur Balance		Residue After Extraction		Ferric Chloride Leach Solution After Reaction							
Exp No	Pyrite[a] wt g	Fe mM	S mM	$FeCl_3$ Conc $\underline{M}$, v (l)	HCl Conc $\underline{M}$	Fe^{+2} mM	Fe^{+3} mM	Total Fe mM	Reaction Time hrs	S as FeS_2 mM	S Free Elemental mM	S as Sulfate mM	Fe_2O_3 mM	FeS_2 mM	Fe^{+2} mM	Fe^{+3} mM	Total Fe mM	% Extraction of Pyrite	S Recovered All Forms %	$SO_4^=/S$ ratio	Fe Recovered[e] All Forms %	$\frac{Fe^{++}(\text{actual})^{g}}{Fe^{++}(\text{calc.})^{f}}$
11[b]	2.0	15.0	30.0	0.15,0.2	1.0	0.4	32.0	32.4	6.0	21.5	3.6	5.6	0.0	10.7	35.8	0.8	36.6	25.5	102	1.4	99.8	1.01
12[c]	2.0	15.0	30.0	0.15,0.2	1.0	0.4	32.0	32.4	6.0	21.5	2.6	5.7	0.0	10.7	36.0	1.4	37.4	25.5	98.7	1.9	101.5	1.05
13	2.0	15.0	30.0	0.6,0.2	0.0	1.2	108.5	109.7	6.0	13.0	4.0	22.2	0.1	6.5	87.5	32.2	119.7	51.0	97.3	2.6	101	1.20
14	2.0	15.0	30.0	1.2,0.2	0.0	1.0	231.3	232.3	6.0	8.2	3.3	11.5	0.0	4.1	83.4	164.0	247.4	64.4	78.8	3.0	102	1.05
15	2.0	15.0	30.0	2.4,0.2	0.0	34.5	484.0	518.5	6.0	15.6	3.6	9.6	0.0	7.8	104.2	415.0	517.2	43.2	96.0	2.2	99.0	----
16	2.0	15.0	30.0	3.6,0.2	0.06	0.5	745.0	745.5	6.0	9.0	3.3	8.0	0.1	4.5	48.6	701.5	750.1	62.2	67.2	1.9	99.3	----
17	2.0	15.0	30.0	1.0,0.2	0.50	0.1	202.6	202.8	6.0	7.7	3.8	10.6	---	7.7	68.5	139.5	208.0	43.6	99.0	2.4	99.1	.94
18	2.0	15.0	30.0	1.0,0.2	0.25	0.1	210.0	210.1	6.0	7.3	3.5	10.5	---	7.3	71.3	140.1	211.4	46.3	95.1	2.5	97.2	1.00
19[b]	2.0	15.0	30.0	1.0,0.2	0.5	0.1	202.6	202.7	6.0	7.4	4.7	9.2	---	7.4	63.9	138.8	202.7	45.2	96.0	1.7	96.6	1.00
20[c]	2.0	15.0	30.0	1.0,0.2	0.5	0.1	202.6	202.7	6.0	7.2	4.6	10.2	---	7.2	71.6	134.2	205.8	46.8	97.1	1.9	97.9	1.01
21[d]	3.00	25.3	50.7	1.0,0.3	0.5				18.0	16.6	17.5	16.0						67	99.0	0.9		
22[d]	3.00	25.3	50.7	1.0,0.3	0.5				18.0	16.7	10.1	23.0						67	98.7	2.3		

[a] Pyrite mineral pulverized to -200 mesh, analyzed 89.8% as $Fe_{2.00}$, the balance is silica and alumina with trace amounts of Zn, and Cu, 1.7 mM HCl soluble sulfate in untreated standard 2.00 g pyrite sample.

[b] 200 ml toluene added to leach solution.

[c] 200 ml tetrachloroethylene added to leach solution.

[d] Attempted steam distillation of sulfur from reaction mixture.

[e] FeS_2, Fe_2O_3, Fe^{+3}, Fe^{+2}.

[f] Calculated on the basis of sulfur and sulfate produced.

[g] Based on Fe^{++} analysis.

both involve rapid removal of sulfur from the potential reaction area, while the use of complex ions may modify the redox potential of the ferric-ferrous couple so that oxidation of sulfur to sulfate will be thermodynamically unfavorable.

The effect of an added organic sulfur solvent on the course of the reaction is shown in Runs 1 and 5 (tetrachloroethylene), Runs 9, 11 and 12 (toluene and tetrachloroethylene), and Runs 17, 19 and 20 (toluene and tetrachloroethylene). The runs are not exactly comparable in all cases, but several conclusions emerge. Runs 1 and 5 show increased conversion from 49% to 65% due to the presence of a sulfur solvent, while in Runs 17, 19 and 20 there is no change. It also appears that the concurrent presence of a sulfur solvent reduces the $SO_4^=$/S ratio. In Runs 1 and 5, the ratio drops from 3.2 to 1.9 and in Runs 17, 19 and 20, it drops from 2.4 to 1.8 ±.1.

Another approach to lower the $SO_4^=$/S ratio is illustrated in Runs 21 and 22 and involves a modified method of steam distilling the sulfur from the reaction mixture before it can react to sulfate. This is accomplished by vigorously refluxing the ferric chloride solution and condensing the sulfur on a large cold finger. The experimental method is not ideal since the sulfur tends to wash back into the flask which is reflected in the $SO_4^=$/S ratios of 2.3 and 0.9 for repeat runs. The latter value corresponds to the formation of 52% sulfur. It is possible that high pressure steam passed through the vessel with an efficient sulfur trap or extraction system would result in very high sulfur recoveries.

A number of extractions were performed to evaluate the effect of anion variations on dissolution of pyrite with ferric ion. The results of these extractions are shown in Table 5.

Extractions (Table 5) run in phosphate media (Runs 23 and 24) were unsuccessful due to precipitate formation at the concentrations necessary for reaction while ammonium citrate and oxalate extractions (Runs 25 and 26) showed such a low rate of dissolution that accurate extraction and $SO_4^=$/S ratio measurements were not obtained.

Ferric nitrate and ferric ammonium sulfate (Runs 27-28) were also tried as examples of the use of other anions. Ferric nitrate gives 92% dissolution of pyrite but essentially all the sulfur is converted to sulfate.

Table 5. Effect of Anion Variation on Extraction of Iron Pyrite (FeS_2)[a]

Exp. No.	Pyrite Weight (grams)	Concentration M, V (1)	Reagent	% Extraction of Pyrite
23	2.0	---,0.2	1M H_3PO_4 0.5M $FeCl_3$	---
24	2.0	---,0.2	1M H_3PO_4 1M Na_3PO_4 0.5M $FeCl_3$	---
25	2.0	0.5,0.2	Ferric Ammonium Citrate	<10
26	2.0	0.5,0.2	Ferric Ammonium Oxalate	<10
27	2.0	0.5,0.2	$Fe(NO_3)_3$	91.8
28	2.0	0.5,0.2	Ferric Ammonium Sulfate	---
29	2.0	0.45,0.2	Ferric Sulfate	56
30	2.0	0.45,0.2	Ferric Sulfate	56

[a] 6 hour retention time at approximately 100°C.

This, together with the absence of ferrous ion in the leach solution indicates that the active reagent was nitric acid formed by hydrolysis of the salt. Ferric ammonium sulfate is unstable at the concentrations needed for reaction and results in a precipitate formation and a low yield. Ferric sulfate (Runs 29-30) dissolved pyrite at a rate almost identical to that of ferric chloride. The sulfur make was approximately the same as that obtained with ferric chloride at similar conversion, indicating a similar final sulfate to sulfur ratio.

The reaction of ferric salt solutions with several sulfide minerals was investigated in order to determine the effect of sulfide mineral structure and/or metallic ions on the forms of sulfur in the product (Table 6). It appeared that there may be a strong influence of either dissolved metal or mineral structure on the sulfate to sulfur ratio. For example, the work of Haver and Wong (7) showed that the dissolution of chalcopyrite ($CuFeS_2$) with aqueous ferric chloride gives elemental sulfur as virtually the only sulfur product.

Table 6. Sulfide Mineral Leaching with Ferric Salt Solutions[a]

Run	Mineral	Ferric Salt	%Mineral Reacted	Sulfate/Sulfur
1	Pyrite, FeS_2	$FeCl_3$	53	2.4
2	Troilite, FeS	$FeCl_3$	47	<.1
3	Chalcocite, Cu_2S	$FeCl_3$	81	<.1
4	Chalcopyrite, $CuFeS_2$	$FeCl_3$	40	<.1
5	Pyrite, FeS_2 (2mM Cu^{+2} added)	$FeCl_3$	82	3.1
6	Pyrite, FeS_2	$Fe_2(SO_4)_3$	56	.8
7	Pyrite, FeS_2	$Fe_2(SO_4)_3$	56	1.00

[a]Conditions: 10 mM sulfide sulfur, 200 ml 0.9M $FeCl_3$ or 0.9N $Fe_2(SO_4)_3$, 6 hours reaction time at 100°C.

Three common sulfide minerals - troilite, chalcocite and chalcopyrite - were extracted with aqueous ferric chloride under the same conditions as a sample of pyrite (Runs 1-4, Table 6). The results show that, with the exception of chalcocite, all minerals were consumed at about the same rate with only pyrite showing a significant amount of sulfate formation. Thus, the formation of sulfate appears to be a peculiar property of pyrite. Dissolved cupric ion plays no role in inhibiting the formation of sulfate (Run 5) although it does apparently increase the mineral conversion.

The effect of sulfate ion on the oxidation of pyrite is shown in Runs 6-7, in which the conversions are similar to ferric chloride extraction although the sulfate to sulfur ratio appears to be lower. However, these ratios may be low since they are based on isolation of elemental sulfur whereas in the other runs the ratios were based upon analyses of both sulfate and sulfur forms.

3.2.2.2 Removal of Pyritic Sulfur from Coal

A laboratory evaluation of the chemical removal of sulfur from coal was performed prior to initiation of bench-scale testing, in order to provide basic coal extraction parameters for efficient bench-scale operation. Four coals were selected (Section 3.1) for laboratory evaluation of chemical techniques for removing pyritic sulfur. Analyses of these four coals samples are shown in Table 7. The indicated tolerances are the standard deviations. Five or more coal samples were used for sulfur, ash, and heat content analyses while three or more samples were used for sulfur forms analyses.

Table 7. Dry Analyses of Coals

	Lower Kittanning	Illinois No.5	Pittsburgh	Herrin No.6
Pyritic Sulfur	3.58 ± .08	1.57 ± .03	1.20 ± .07	1.65 ± .04
Sulfate Sulfur	0.04 ± .01	0.05 ± .01	0.01 ± .01	0.05 ± .01
Organic Sulfur	0.67 ± .10	1.86 ± .04	0.68 ±0.10	2.10 ± .06
Total Sulfur	4.29 ± .06	3.48 ± .03	1.88 ± .07	3.80 ± .04
Ash	20.77 ± .59	10.96 ± .26	22.73 ± .48	10.31 ± .28
Btu	12,140 ± 80	12,801 ± 58	11,493 ± 60	12,634 ± 55
Rank	Medium Volatile Bituminous	High Volatile B Bituminous	High Volatile A Bituminous	High Volatile B Bituminous

Ferric chloride and ferric sulfate were selected as the most promising iron salts for removal of pyrite from coal on the basis of the results obtained in the previous section (i.e., these salts gave the highest rate of pyrite dissolution coupled with the highest elemental sulfur make).

The extent of the reaction indicated by eq 1 (pg.12) relative to that of eq 2 (i.e., the sulfate to sulfur ratio) is 2.4 ±.2 when reacting mineral pyrite and 1.4 ±.4 when reacting pyrite found in the coals used in this work. Although both materials have the same formula and crystal structure, differences in reactivity have been documented and have been attributed to inpurities and crystal defects peculiar to the modes of formation of the various pyrites (8). In the case of coal, no significant variation of this ratio with ferric ion concentration, acid concentration, coal seam or reaction time was found. The results for each coal are shown in Table 8.

Table 8.

Sulfate to Sulfur Ratio for Extraction of Coal and Mineral Pyrite with Ferric Chloride Solution

Substrate	Sulfate to Sulfur Ratio (Average of All Runs)
Mineral Pyrite	2.4 ± .2[a]
Lower Kittanning	1.4 ± .3
Illinois No.5	1.6 ± .4
Pittsburgh	1.3 ± .3
Herrin No.6	1.4 ± .3

[a] Standard deviation

A parametric study was made in order to determine the effect of acid concentration, coal particle size, ferrous ion and sulfate ion concentrations, and reaction time on pyrite removal. These parameters were studied using conditions that gave 40%-70% pyritic sulfur removal so that the effects of parameter variations would be clear. In addition, studies were performed to demonstrate 90%-100% pyritic sulfur removal with both ferric chloride and sulfate and a set of experiments was designed to point up differences between ferric sulfate and ferric chloride (the two major candidate iron salts). The extractions were performed in glass apparatus at atmospheric pressure with mixing provided from an overhead motor stirrer. The residual leach solution was removed by washing with hot water and the elemental sulfur was removed by washing with hot toluene. The coal was then dried in a vacuum oven to constant weight. The summary tables shown and discussed on the pages which follow are supplemented by complete data tables in Appendix A, Volume 2 - Laboratory Experimentation.

The effect of added hydrochloric acid concentration was studied in order to determine the effect of acid on pyrite and ash removal, sulfate/sulfur ratio, and final heat content. Since coal has many basic ash constituents, increased ash removal was expected as well as suppression of the sulfate to sulfur ratio, since the reaction that results in sulfate formation also yields 8 hydrogen ions per mole of sulfate ion (common ion effect). Concentrations of 0.0, 0.1, 0.3 and 1.2M hydrochloric acid in 0.9N ferric chloride were studied. Duplicate runs were made at each concentration with all four coals (total of 32 runs). The results showed no clear trends even when the data was smoothed via computer regression analysis. Apparently, the concentration range was not broad enough to have any substantial effect on the production of sulfate or the removal of ash.

An important consideration in any chemical process is the selectivity for the desired reaction. In the case of oxidative leaching of pyrite by ferric ion, the extent of reaction of the reagent with the coal matrix has a major effect on the process economics. We have found that the extent of this reaction varies from small to substantial depending on the acid concentration, coal bed, and ferric salt anion. In order to define this effect quantitatively, the ratio of actual millimoles of ferrous ion produced to the millimoles of ferrous ion generated by production of sulfate and elemental sulfur from pyrite dissolution was calculated for each run. This ratio, Fe(II)[Experimental]/Fe(II)[Calculated], has a value of one for 100% selectivity and a higher value for less than 100% selectivity. Selectivity data in Table 9 for ferric chloride were smoothed by linear regression analysis using the values generated in the acid test matrix (described in preceding paragraph) while the ferric sulfate data were the average of triplicate runs.

Table 9.

Variation of Ferric Ion Consumption with Acid Concentration and Ferric Salt Anion

Coal	Fe(II)[Expt]/Fe(II)[Calc]		
	$0.9\underline{N}$ $FeCl_3$		$0.4\underline{N}$ $Fe_2(SO_4)_3$
	$0.0\underline{M}$ HCl	$1.2\underline{M}$ HCl	$0.0\underline{M}$ H_2SO_4
Lower Kittanning	1.2	1.4	1.2
Illinois No.5	3.8	6.6	1.6
Pittsburgh	2.2	3.4	1.5
Herrin No.6	3.7	6.4	2.4

It is readily apparent that the higher ranked Appalachian (Lower Kittanning and Pittsburgh) coals react to a lesser extent with ferric ion under all experimental conditions than the lower ranked Eastern interior (Illinois No.5 and Herrin No.6) coals. In addition, the ferric chloride runs show that a very substantial acid catalyzed reaction occurs which is most evident for the Illinois No.5 and Herrin No.6 coals. In these coals, a reduction of about 42% in ferric ion consumption is observed when the starting HCl concentration is reduced from $1.2\underline{M}$ to $0.0\underline{M}$. The corresponding reduction for Pittsburgh and Lower Kittanning coals are 35% and 14% respectively. When ferric sulfate is used, further reductions in ferric ion consumption ranging from 3% for Lower Kittanning coal to 63% for Illinois No.5 coal are observed. From these early data, it appears that ferric sulfate is the preferred form of ferric salt to increase selectivity. In addition, bench-scale experimentation (Section 3.2.3) shows further improvements in selectivity for ferric sulfate leaching.

The data listed in Table 10 illustrate the effect of coal top size on pyritic sulfur removal. The coal samples were prepared by the same comminution techniques and, consequently, the size distribution of the samples should be similar for each coal (9). In general, an increase of pyrite removal is observed for smaller top sizes as expected due to exposure of pyrite encapsulated within the coal matrix. The Illinois No.5 and Herrin No.6 coals deserve special comment because reaction of the ferric ion with the coal matrix resulted in greater than 75% depletion of the reagent. For the No.5 coal this effect was approximately the same for all three sizes and the

Table 10.
Effect of Coal Top Size on Pyritic Sulfur Removal

Coal	Sulfur Removed[a] -1/4	-14	-100
Lower Kittanning	35	60	65
Illinois No.5	45	35	50
Pittsburgh	--	45	60
Herrin No.6	--	70	50

[a] Values rounded to nearest 5%.

resulting depletion of the reagent may have had a leveling effect on the results. In the case of the No.6 coal, substantially less ferric ion was consumed by the -14 mesh coal than by the -100 mesh coal (68% vs >95%) which is probably the reason for the increased removal. Thus, while the use of a larger coal top size reduces pyrite removal, removals are not a strong function of mesh size. It is expected that the internal surface characteristics and the permeability of coal to aqueous media are important factors controlling desulfurization, along with the surface exposure of pyrite caused by grinding. The coal top size may have an effect on the ultimate amount of pyrite removal, and further research is necessary to clarify the exact nature of this effect.

Since the use of ferric sulfate in a process has several advantages over ferric chloride, a test matrix (summarized in Table 11) was performed to compare the ability of ferric sulfate to remove pyritic sulfur from all four coals. Utilizing solutions 0.4N in ferric ion, it was found that slightly less sulfur was removed by ferric sulfate than was indicated with ferric chloride. However, when a solution of 0.09N ferric ion was used, it was found that ferric sulfate removed an equal or greater amount of sulfur than ferric chloride. Analysis of each coal also showed that a small amount of sulfate remains with the coal after a simple washing procedure. Preliminary results show that this can be reduced to starting values by using more rigorous washing procedures. Assuming that all the residual sulfate can be removed, then the values for sulfur removal by ferric sulfate extraction can be raised 3% to 9% depending on the coal.

Table 11.

Comparison of Ferric Sulfate and Ferric Chloride for Pyrite Removal[a]

Coal	Pyritic Sulfur Removed % w/w				Ferric Sulfate Treated Coal (0.4N Fe^{+++}) % w/w Sulfate		Removal Correction abs %[b]
	0.4N Fe^{+++}		0.9N Fe^{+++}				
	Cl	SO_4	Cl	SO_4	Initial	Final	
Lower Kittanning	43	38	43	54	0.07	0.17	+3
Illinois No.5	48	43	50	50	0.05	0.17	+8
Pittsburgh	50	33	58	--	0.01	0.08	+7
Herrin No.6	35	33	52	64	0.05	0.20	+9

[a] Conditions: 600 ml and 0.9N Fe^{+3} solution, 100 g 100 mesh top size coal, refluxed at 100°C for 2 hours.

[b] Increase ferric sulfate extraction values by this % to correct for retained sulfate.

A multiple batch leaching mode was evaluated next as it is a simple laboratory procedure and at the same time it could approximate conditions encountered in a commercial plant. A 1-hr per batch leach time was used because our 2-hr results indicated that in the early stages of removal the rate begins to tail off after 1 hour. Six leaches (or batches) per run were used in order to assure that any pyrite that could be removed in a reasonable amount of time would be removed. The progress of removal was monitored by analyzing the sulfate content in each batch of spent leach solution, while elemental sulfur was not removed until all leaches were completed. Table 12 shows pyrite extraction with ferric chloride during each successive leach as monitored by sulfate analysis of the leach solution. Note that the major portion of pyritic sulfur is removed in the first two leaches or in two hours reaction time, followed by lesser amounts in the third and fourth leaches and only small amounts in the final two leaches.

Table 12.

Pyrite Extraction with Ferric Chloride as a Function of Successive Leaches

	Lower Kittanning	Pittsburgh	Illinois No.5	Herrin No.6
Initial Pyritic Sulfur, mmol	102	37.5	43.4	49.7
Extracted Pyritic Sulfur as Sulfate[a]				
mmol 1	31.2	13.5	11.4	12.5
2	12.4	6.0	5.5	6.3
3	9.2	4.6	3.6	5.0
4	4.8	2.1	1.8	2.1
5	0.4	0.6	0.7	1.0
6	0.3	0.3	0.5	0.6

[a] A nominal 40% of the pyritic sulfur remains with the coal as elemental sulfur. All indications are that the sulfur to sulfate ratio is constant.

The results in terms of final sulfur values and pyrite removal are given in Table 13. Note that pyritic removal computed from either sulfur forms analyses or the difference in total sulfur between processed and untreated coal (Eschka analysis) resulted in essentially identical values of 93-98% and 95-107%, respectively. This corresponds to total sulfur removal of 40-80%. The observation of greater than 100% removal is due to cumulative error in analysis and to removal of small amounts of sulfate (0.02-0.04%).

Multiple pass experimentation was performed using ferric sulfate leach solution for treatment of Lower Kittanning and Pittsburgh coals (Table 14) in order to compare the potential of ferric sulfate to totally remove iron pyrite from coal. The overall retention time was 8.5 hours for these experiments with complete changes of leach solution at 1.0 and 4.5 hours.

Table 13. Pyritic Sulfur Removal with Ferric Chloride[a]

Coal	Total Sulfur Analysis				Pyritic Sulfur Analysis[c]		
	Start, %	Finish, %	Total S[b] Removal, %	Pyritic S Removal, %	Start, %	Finish, %	Pyritic S[b] Removal, %
Lower Kittanning	4.32	0.93	78	95	3.58	0.06	98
Pittsburgh	1.88	0.75	60	95	1.20	0.09	93
Illinois No.5	3.48	1.88	46	102	1.57	0.10	94
Herrin No.6	3.80	2.04	46	107	1.65	0.05	97

[a] 6 1-hour leaches with fresh 1M $FeCl_3$ (0.1M HCl).

[b] Assuming total sulfur removal = $\frac{S_o - S_f}{S_o} * 100$, where S_o = percent sulfur content at start and
S_f = percent sulfur content after extraction

[c] Based on sulfur forms analysis.

The results shown in Table 14 indicate that 100% removal of pyritic sulfur was obtained for both coals while 75% and 40% of the total sulfur was removed from Lower Kittanning and Pittsburgh coal, respectively. The sulfate content of the coals was slightly increased. It is presumed that a more thorough washing would remove additional sulfate and slightly increase the overall sulfur removal.

Table 14.

Complete Removal of Pyrite Using Ferric Sulfate[a]

Coal[b]	Pyritic Sulfur % w/w			Sulfate Sulfur % w/w		Total Sulfur % w/w		
	Initial	Final	Removal	Initial	Final	Initial	Final	Removal
Lower Kittanning	2.58	0.02	100	0.04	0.16	4.29	1.10	75
Pittsburgh	1.20	0.00	100	0.01	0.21	1.88	1.12	40

[a] $1.0\underline{N}$ $Fe_2(SO_4)_3$, 1.2-1.8 ℓ per pass, 100°C reaction temperature

[b] -100 mesh coal, 200 g samples

Research on ferric chloride extraction of Lower Freeport coal, performed as a part of a TRW sponsored process chemistry feasibility demonstration in 1971, indicated that the chloride content of the treated coal was the same as that of the starting coal. However, in our present effort it soon became apparent, due to variable mass balances and final btu values, that our nominal laboratory washing procedure left a variable (sometimes considerable) amount of chloride on the coal and that the Illinois No.5 and Herrin No.6 coals retained more chloride than the Pittsburgh or Lower Kittanning coals. A random sampling analysis (Table 15) showed that the residual chloride level ranged from 0.61% to 3.06%.

Preliminary experiments were begun using more extensive washing which gave final chloride contents of 0.40% to 1.40% (Table 15). More thorough washing was expected to reduce this value even more, but concurrent experiments with ferric sulfate showed that a consistent 0.08% to 0.20% sulfate is left on the coal with only filter funnel washing and a final short soak. Thus, the use of ferric sulfate is advantageous to the

Table 15.

Residual Ferric Salt Anions Remaining on Coal After Water Wash

Coal	Ferric Chloride		Ferric Sulfate
	Nominal Wash[a] % Cl w/w Average(Range)	Multiple Batch Wash[b] % Cl w/w	Nominal Wash[c] % SO_4 w/w
Lower Kittanning	.9 (.61-1.40)	.40	0.16
Illinois No.5	2.2 (.68-2.84)	1.22	0.17
Pittsburgh	1.2 (1.26-1.90)	.41	0.21
Herrin No.6	2.3 (1.52-3.06)	1.40	0.20

[a] Average of five or more runs. Filter cake washed on filter with hot water until filtrate colorless.

[b] Average of two runs. Four additional hot water washes with intermediate filtration.

[c] Average of two runs. Filter cake washed on filter with hot water until filtrate colorless.

process in allowing a moderate washing cycle for removal of most of the residual iron salts, while the small iron sulfate residues noted to date have the effect of only slightly decreasing the amount of overall sulfur removal.

3.2.2.3 Regeneration of Ferric Sulfate Leach Solution

A preliminary laboratory effort was initiated to investigate ferrous ion regeneration with oxygen in order to provide the basic reaction information necessary for efficient bench-scale testing. The basis for the experimental approach was a Russian paper (10) which shows that the rate expression for ferrous ion conversion is (eq 6):

$$-\frac{d[Fe(II)]}{dt} = K'[O_2]\,[Fe(II)]^2 \qquad (6)$$

where $K'[O_2]$ can be set equal to K when the reactions are run under conditions of constant oxygen contact with the aqueous solution (eq 7):

$$-\frac{d[Fe(II)]}{dt} = K\,[Fe(II)]^2 \qquad (7)$$

which yields on integration (eq 8):

$$\frac{1}{[Fe(II)]} = Kt + C \qquad (8)$$

Since K depends on effective oxygen concentration, catalysts, inhibitors, etc., its value is dependent on any factors that alter the equilibrium concentration of oxygen and extracted or added metals ion in solution. The effective oxygen concentration is an empirical value which depends on the solubility, bubble size, residence times, and other factors (see Section 3.2.3).

Table 16 shows the results of *ex situ* regeneration studies using spent ferric sulfate solution from pyrite dissolution of the pure mineral, Lower Kittanning coal, and Illinois No.5 coal. The rate constants were calculated from the straight line obtained by plotting 1/[Fe(II)] vs time (Figures 4 and 5). The data show that the rate is faster at 100°C than at 60°C (Runs 1-2 and 4-5) even though the reduced oxygen solubility at the higher temperature could be expected to lower the rate. Note also that the spent solution from the mineral pyrite and Lower Kittanning coal runs react at comparable rates (Runs 1 and 3) while the solution from Illinois No.5 coal reacts at twice the rate of mineral pyrite solution (Runs 2 and 8), perhaps due to extracted ions acting as catalysts.

The effect of copper catalysis was carefully studied for Lower Kittanning leach solutions as this ion was shown (10) to catalyze the oxidation of ferrous ion. From a process standpoint, a small concentration of copper ion could be continually recycled with the leach solution at little or no process cost.

The results are shown graphically in Figures 4 and 5 where it can be seen that cupric ion is effective and the rate constant levels off at cupric ion concentrations higher than 0.05M.

Several other ions were tried in order to test their catalytic effect (Table 16 and Figure 6). The results listed for Runs 8-12 for Illinois No.5 solution indicate that Ni(II), Cr(II) and Zn(II) have no significant effect at 0.05M concentration while Mn(II) approximately doubles the rate. It should be noted that the estimated rate for 0.05M Cu(II) at 100°C and solution from Lower Kittanning coal leaching is ca. 8.5 times the standard solution.

Table 16. Calculated Rate Constants for Ferric Ion Regeneration[1]

Run	Fe^{+2}	Catalyst		Temp. (°C)	K (10^{-4} $\frac{liter}{mole\text{-}min}$)	Origin of Solution
	Molarity	Cation	Molarity			
1	0.152	Neat	--	60°	21	$Fe_2(SO_4)_3$ Reaction with FeS_2
2	0.138	Neat	--	100°	24	$Fe_2(SO_4)_3$ Reaction with FeS_2
3	0.174	Neat	--	60°	21	Lower Kittanning Coal
4	0.169	Cu^{+2}	.050	60°	55	Lower Kittanning Coal
5	0.155	Cu^{+2}	.050	100°	170	Lower Kittanning Coal
6	0.173	Cu^{+2}	.013	100°	146	Lower Kittanning Coal
7	0.169	Cu^{+2}	.003	100°	120	Lower Kittanning Coal
8	0.109	Neat	--	100°	51	Illinois No.5 Coal
9	0.115	Ni^{+2}	.050	100°	53	Illinois No.5 Coal
10	0.115	Mn^{+2}	.050	100°	103	Illinois No.5 Coal
11	0.115	Cr^{+3}	.050	100°	53	Illinois No.5 Coal
12	0.115	Zn^{+2}	.050	100°	59	Illinois No.5 Coal

[1] Conditions: 200 ml of spent ferric sulfate solution were brought up to temperature in a 500 ml three-neck flask equipped with a reflux condenser, thermometer and a gas dispersion tube.

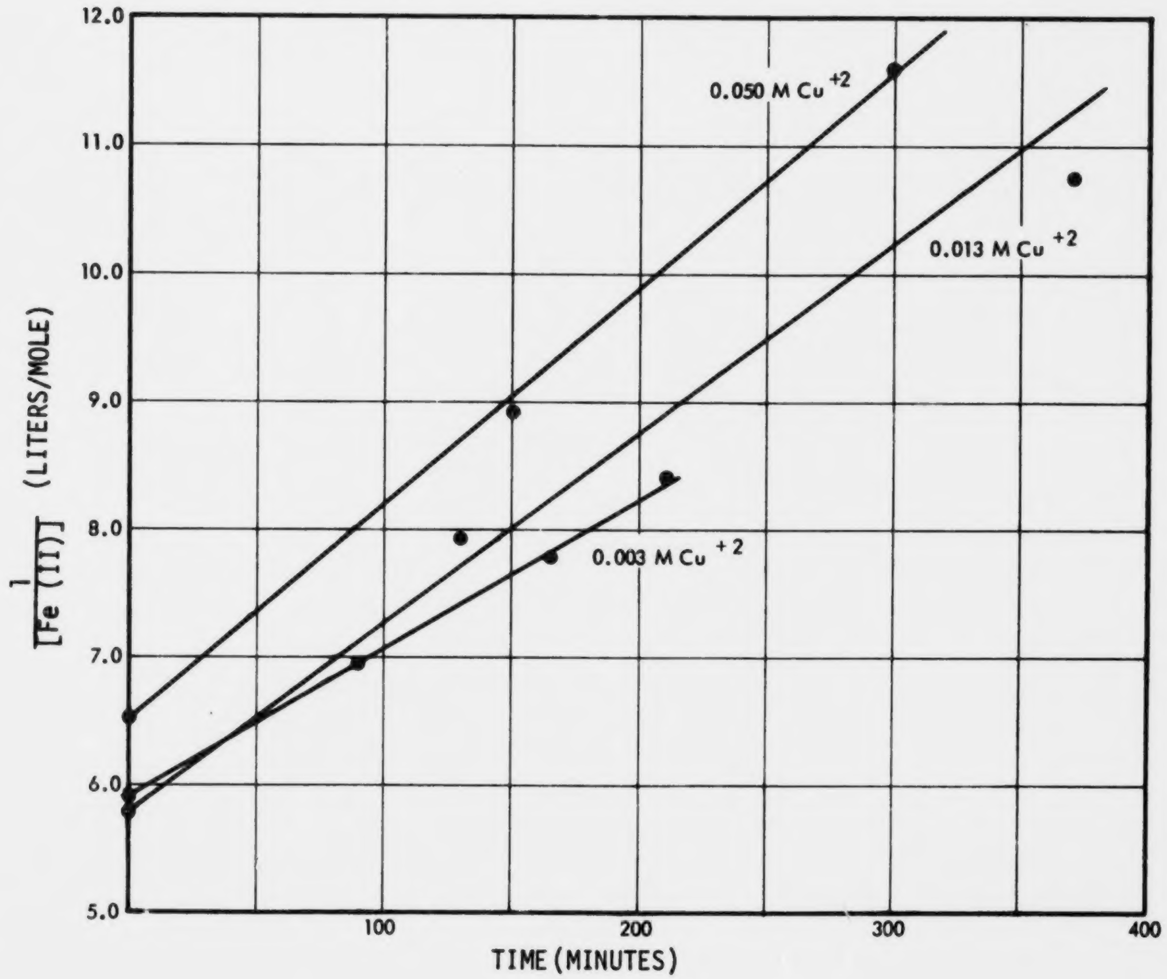


Figure 4. Effect of Copper Ion Concentration on Ferric Ion Regeneration at 100°C

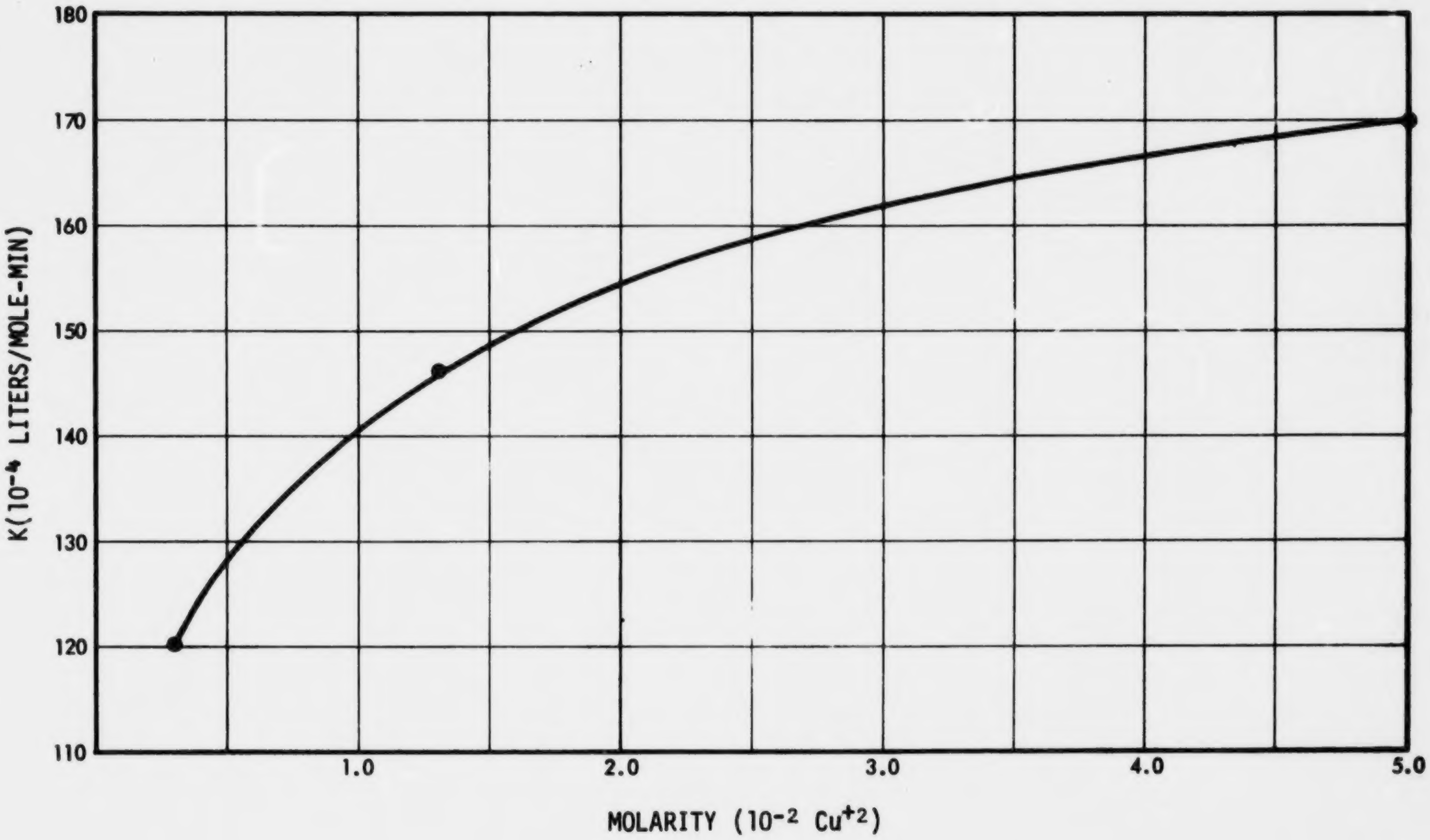


Figure 5. Effect of Cu(II) Ion Concentration on the Rate Constant for Ferric Ion Regeneration at 100°C

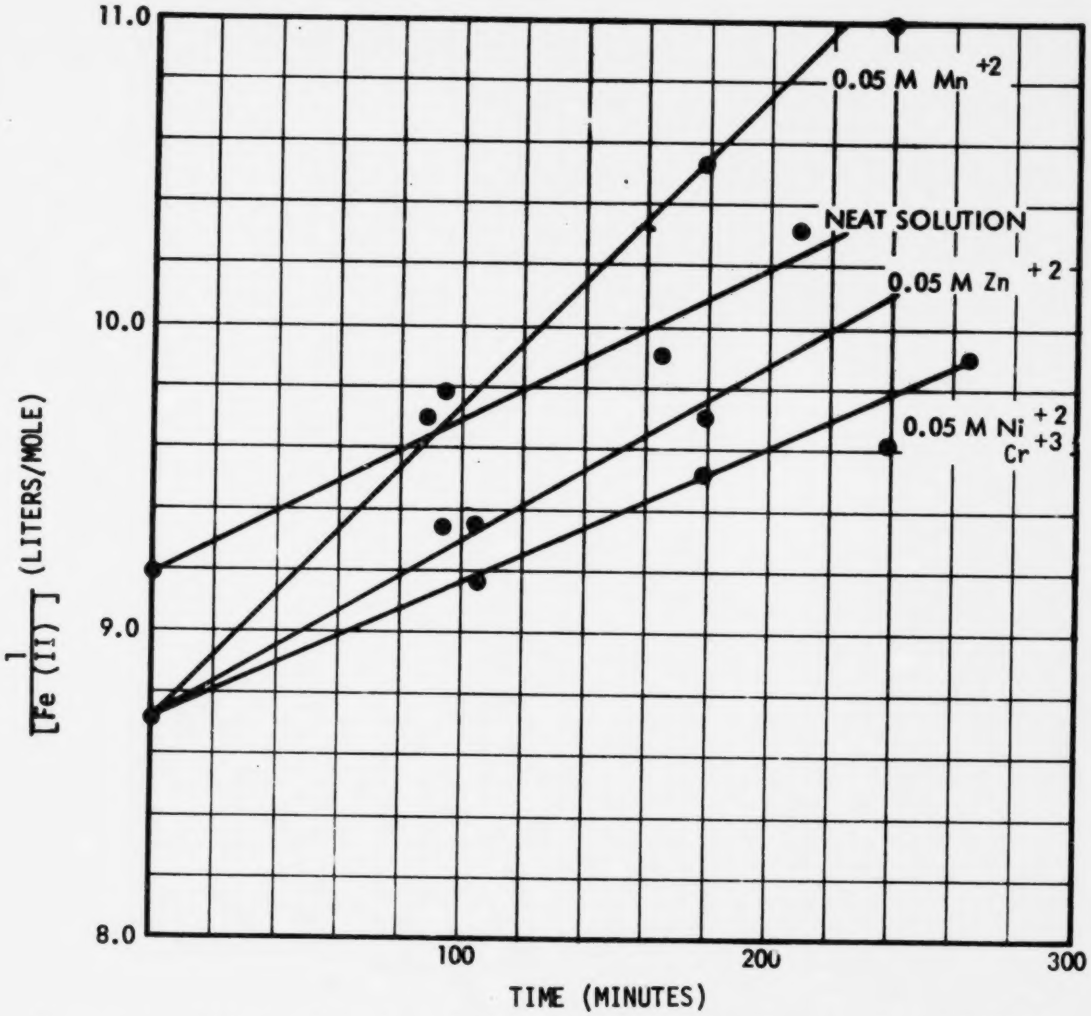


Figure 6. Effect of Various Cations on Ferric Ion Regeneration at 100°C

3.2.2.4 Concurrent Coal Leaching and Spent Leach Solution Regeneration

A matrix of duplicate experiments was performed with Illinois No.5 coal to investigate concurrent regeneration of ferric sulfate solution during the coal leach step. The nominal reaction conditions and results are given in Table 17, and the full data base is presented in Appendix A, Volume 2. The average pyritic sulfur removal for all runs is 69.0% ± 4.0% which is similar to the removal experienced with no regeneration. This implies that oxygen itself does not measurably react with iron pyrite under these conditions. No statistical difference could be found between any two sets of duplicates. With equal sulfur removal noted and assuming constant sulfate/sulfur ratio, the degree of regeneration can be calculated from the final ferrous ion concentration (corrected for differences in coal weight) and a standard in which oxygen (no catalyst) is replaced by nitrogen.

Note that there is no difference in regeneration when a medium pore size frit is used in place of the fine size frit (Runs 11-12 compared to Runs 5-6) even though reduced regeneration was expected since the larger bubbles should result in less efficient contact with the solution. Reduction in oxygen flow rate (Runs 7-8) reduced regeneration as would be expected. However, by far the largest amount of regeneration (60-65%) occurred at lower than reflux temperature (Runs 13-16) and was probably due to increased oxygen solubility. In addition, pyrite removal was not reduced during reactions in the temperature range 65-85°C, possibly due to the higher ferric ion concentration which was maintained, while at 50°C the pyritic sulfur removal fall-off was significant. Preliminary data indicates that no measurable oxidation of the sulfur made from pyrite conversion is occurring due to the oxygen present under the reaction conditions. Comparison of coal heating values before and after leaching with and without regeneration did not indicate any copper ion or oxygen effects on the oxidation of coal.

The use of a small amount of copper catalyst (compare Runs 3-4 and 5-6) appears to increase the rate of regeneration by about 30% relative. From a process standpoint, this would mean adding a small initial charge of copper sulfate which would simply recycle continually with the leach solution. On the other hand, the need for copper salts might well be

TABLE 17. SUMMARY OF IN-SITU REGENERATION OF FERRIC SULFATE LEACH SOLUTION[a,b].

Run	Special Conditions	Final % S (% w/w)	Final SO_4, (% w/w)	Pyritic sulfur removed (%)	Fe^{+3} used (% w/w)	Heat content[c] after treatment (rel %)	% Regeneration
1-2	N_2 flow, no catalyst	2.60	.25	68.8	17.3	97.5	0[d]
3-4	No catalyst	2.59	.26	70.1	14.0	96.4	15
5-6	Nominal, 95°C	2.70	.30	65.6	13.6	97.1	19
15-16	Nominal, 80°C	2.58	.18	68.5	5.8	97.6	62
9-10	Nominal, 65°C	2.66	.32	67.7	6.3	96.5	60
13-14	Nominal, 50°C	2.85	.14	45.9	3.5	97.7	65
7-8	50 ml/min O_2 flow	2.65	.32	69.4	14.4	98.2	1
11-12	Medium Frit	2.58	.27	68.8	12.2	96.9	25

[a] All values are averages of duplicate runs.

[b] 100 g - 100 mesh Illinois No.5 coal heated at 95°C with 2.4 liters 1.0$\underline{N}$ ferric sulfate, 0.05$\underline{M}$ in $CuSO_4$ for 4 hours, with an oxygen flow of 200 ml/min through a fine fritted glass.

[c] Btu corrected for ash content and btu associated with pyrite (2,995 btu/lb).

[d] Baseline value.

replaced by trace elements picked up during repeated coal extraction or by more efficient gas-liquid contactor equipment (see Section 3.2.3).

3.2.3 Bench-Scale Experimental Results

Following the initial laboratory experimentation a detailed bench-scale experimental program was conducted. The bench-scale investigation, which involved a scaling of approximately 6:1 over the laboratory experiments, was aimed at obtaining the quantitative, mass balanced, data necessary for:

(a) performing a preliminary engineering process design and cost analysis, and

(b) designing a pilot plant.

The bulk of experimentation was performed at TRW's Chemistry and Process Development Laboratory at the Capistrano Test Site. A substantial portion of the coal sample analyses was performed by Commercial Testing & Engineering Company (CT&E), Chicago, Illinois, with the remainder performed at TRW's Redondo Beach Chemistry Laboratories.

Two coals were investigated at bench-scale: Lower Kittanning and Illinois No.5. Since the two coals differ substantially in rank and sulfur form content (see Table 1), they offered an excellent means for testing TRW's coal desulfurization process efficiency as a function of coal rank and sulfur form concentration.

Coal samples, ground to -1/4 inch,were furnished in lots of approximately 1200 lbs by the Process Development Department, Bureau of Mines, Pittsburgh, Pennsylvania, and the Illinois State Geological Survey, Urbana, Illinois.

Figure 7 is a block diagram of the basic apparatus utilized for the bench-scale investigations. The apparatus consists of seven unit operation sections which involve coal extraction, solid liquid separation (reagent from coal), reagent regeneration, coal washing, elemental sulfur removal, solvent recovery,and coal drying.

Extensive parametric investigations were performed on the principal unit operations of the process with special emphasis placed on the coal leaching and regeneration units. Two leaching reagents, ferric chloride and ferric sulfate,were studied.

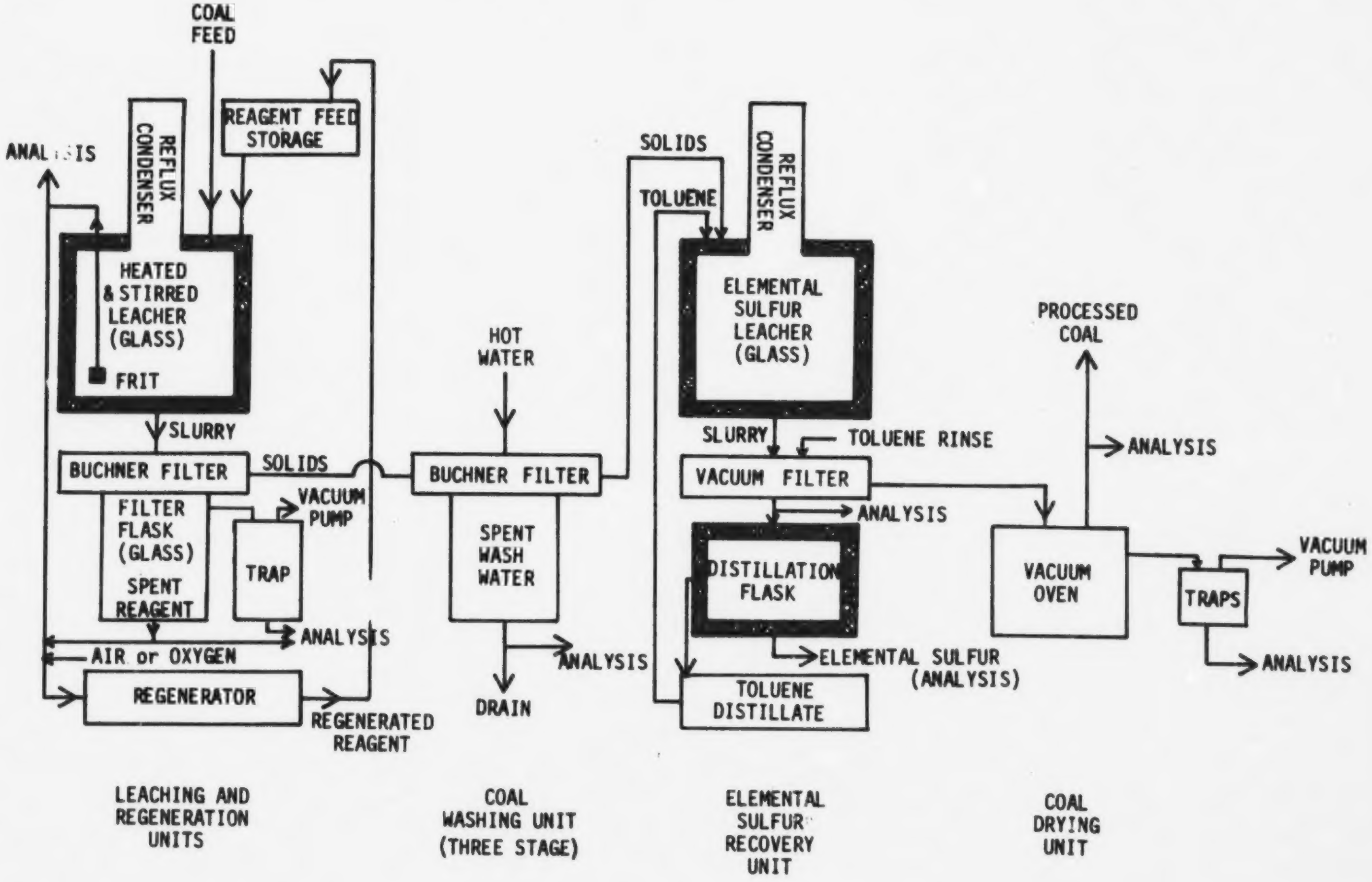

COAL FEED
REFLUX CONDENSER
REAGENT FEED STORAGE
ANALYSIS
HEATED & STIRRED LEACHER (GLASS)
FRIT
SLURRY
BUCHNER FILTER
SOLIDS
FILTER FLASK (GLASS)
SPENT REAGENT
VACUUM PUMP
TRAP
ANALYSIS
AIR or OXYGEN
REGENERATOR
REGENERATED REAGENT
HOT WATER
BUCHNER FILTER
SPENT WASH WATER
ANALYSIS
DRAIN
SOLIDS
TOLUENE
REFLUX CONDENSER
ELEMENTAL SULFUR LEACHER (GLASS)
SLURRY
TOLUENE RINSE
VACUUM FILTER
ANALYSIS
DISTILLATION FLASK
ELEMENTAL SULFUR (ANALYSIS)
TOLUENE DISTILLATE
PROCESSED COAL
ANALYSIS
VACUUM OVEN
TRAPS
VACUUM PUMP
ANALYSIS
LEACHING AND REGENERATION UNITS
COAL WASHING UNIT (THREE STAGE)
ELEMENTAL SULFUR RECOVERY UNIT
COAL DRYING UNIT

FIGURE 7. BASIC BENCH-SCALE PYRITIC SULFUR REMOVAL APPARATUS

Parameters investigated included the following:

- Leacher Unit - coal particle size, extraction temperature, extraction time, reagent residence time, reagent purity, total iron concentration, ferric ion to total iron ratio, coal weathering.
- Solid-Liquid Separation Unit - coal particle size, temperature, solid to liquid ratio.
- Reagent Regeneration Unit - temperature, pressure, total iron concentration, ferrous ion concentration, residence time, oxygen partial pressure, liquid to gas ratio, liquid-gas mixing.
- Washing Unit - coal particle size, water temperature, water volume.
- Elemental Sulfur Removal Unit - residence time.
- Coal Drying Unit - temperature, residence time.

The apparatus and procedures were carefully designed to furnish good process and unit operation mass balances; the data obtained verified the efficiency of the design utilized.

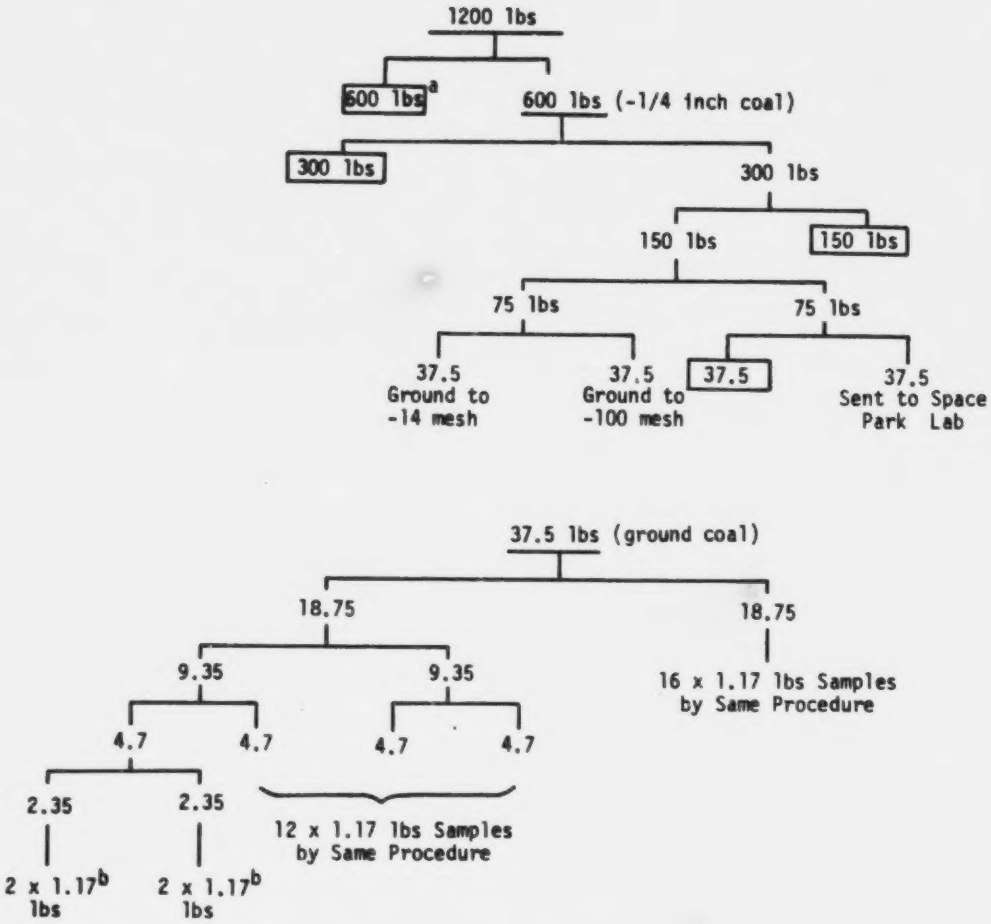
The bench-scale results are described in the three sections to follow.

3.2.3.1 Coal Sampling and Sample Preparation

Sample preparation and storage facilities were set up and sampling procedures were specified to conform with ASTM approved sampling techniques. The sampling facility was housed in a "Sears" 7x10 foot portable building located adjacent to the main laboratory building at the TRW Capistrano Test Site (CTS). The facility housed the laboratory pulverizer (hammer mill type), a "Tyler" sieve shaker, a complete set of sieves, balances, sample splitters, and the bulk of -1/4 inch coal under a helium blanket. A riffled and ground coal storage facility was set up within the main laboratory at CTS; this facility was equipped with a helium gas flushing installation.

The coal sampling procedure is illustrated in Figure 8. The approximately 1200 lb lots of each coal were successively halved by the use of commercial rifflers to approximately 37.5 lb lots. This was the minimum coal lot size for further grinding (-100 mesh and -14 mesh). As indicated in Figure 8 one half of the coal after each riffling was stored under helium. After grinding, each 37.5 lb ground coal lot was riffled by the same procedure (halving) to approximately 500-gram samples which served as the basic sample size for the bench-scale investigation. This procedure is the most commonly used method for coal sampling and it is ASTM approved. However, in order to prove its validity and to establish maximum deviations in sample-to-sample homogeneity, duplicate samples of each of two ground coal lots from each grind size were analyzed for moisture, ash, btu content, total sulfur, sulfur forms, and nitrogen. The results are presented in Table 18. Average values and their standard deviations are reported for each grind size as well as the average of two coal top sizes (100 mesh and 14 mesh).

The entries of Table 18 indicate that moisture, heat content, and sulfate increased slightly with increasing coal top size while total sulfur, organic sulfur, pyritic sulfur, and ash decreased with increasing coal top size. Since all grind sizes (top sizes) originated from the same lot of each coal, the observed differences may be due to losses of moisture and coal powder (low in or free of pyrite) during grinding, despite the precautions taken. The variation in sulfate is not easily justi-


1200 lbs
600 lbs[a]
600 lbs (-1/4 inch coal)
300 lbs
300 lbs
150 lbs
150 lbs
75 lbs
75 lbs
37.5 Ground to -14 mesh
37.5 Ground to -100 mesh
37.5
37.5 Sent to Space Park Lab
37.5 lbs (ground coal)
18.75
18.75
16 x 1.17 lbs Samples by Same Procedure
9.35
9.35
4.7
4.7
4.7
4.7
12 x 1.17 lbs Samples by Same Procedure
2.35
2.35
2 x 1.17[b] lbs
2 x 1.17[b] lbs

(a) Boxed quantities indicate stored lot sizes.

(b) Bench-scale size samples.

FIGURE 8. COAL SAMPLING PROCEDURE

Table 18.

Reproducibility of Coal Sampling Procedure

STARTING COAL ANALYSES, DRY BASIS									
STARTING COAL	COAL TOP SIZE	HEAT CONTENT (BTU/lb)	ASH (wt.%)	TOTAL SULFUR (wt.%)	SULFUR FORMS			Nitrogen (wt.%)	MOISTURE IN "AS RECEIVED" COAL, wt.%
					Organic (wt.%)	Pyritic (wt.%)	Sulfate (wt.%)		
FOUR SAMPLE AVERAGES*									
Illinois No.5	100 mesh	12,687 ±52	11.45 ±0.17	3.61 ±0.10	1.96 ±0.24	1.57 ±0.17	0.08 ±0.02	1.36 ±0.02	9.55 ±0.51
Illinois No.5	14 mesh	12,644 ±93	11.37 ±0.31	3.58 ±0.06	1.96 ±0.06	1.55 ±0.02	0.06 ±0.02	1.33 ±0.04	9.31 ±0.10
Illinois No.5	1/4 inch	12,793 ±66	11.14 ±0.45	3.37 ±0.04	1.80 ±0.10	1.44 ±0.10	0.13 ±0.01	1.34 ±0.04	12.17 ±0.57
Lower Kittanning	100 mesh	12,267 ±125	20.14 ±0.50	4.33 ±0.09	0.71 ±0.10	3.58 ±0.08	0.04 ±0.03	1.19 ±0.09	0.96 ±0.08
Lower Kittanning	14 mesh	12,318 ±59	19.64 ±0.76	4.32 ±0.10	0.64 ±0.13	3.60 ±0.23	0.08 ±0.03	1.13 ±0.09	0.92 ±0.09
Lower Kittanning	1/4 inch	12,392 ±141	19.26 ±0.43	3.94 ±0.16	0.39 ±0.15	3.40 ±0.12	0.14 ±0.01	1.13 ±0.03	1.50 ±0.11
EIGHT SAMPLE AVERAGES**									
Illinois No.5	100 & 14 mesh	12,665 ±75	11.41 ±0.25	3.59 ±0.08	1.96 ±0.17	1.56 ±0.12	0.07 ±0.02	1.35 ±0.03	9.43 ±0.37
Lower Kittanning	100 & 14 mesh	12,292 ±98	19.89 ±0.64	4.32 ±0.10	0.67 ±0.12	3.59 ±0.17	0.06 ±0.03	1.16 ±0.07	0.94 ±0.09

*Deviations were determined from analyses performed at CTS on coal samples of at least two different ground lots.

**These values, representing the average analyses of -100 and -14 mesh coal samples, were used as the "starting coal analysis" during most of the program. Slightly different starting coal analysis values were used(and indicated)when the experimental matrix included -1/4 inch samples or when the starting coal was not completely dry.

fiable. In general, the observed deviations were insignificant to the interpretation of the experimental data and were within ASTM standards. In the rare cases where these deviations were important to data interpretation, adjustments were made and noted.

Table 19 presents data on coal particle size distribution of the selected coals. At least four deteminations were performed on each of the top sizes investigated in the program (1/4 inch, 14 mesh, and 100 mesh). Reproducibility of determinations was excellent. The -14 mesh to -1/4 inch ratio of external surface areas of equal weight coal samples was estimated to be four; that of -100 mesh to -1/4 inch was approximately sixteen. Thus, the -100 mesh coal has approximately four times the external surface area of the -14 mesh coal and 16 times the external surface area of the -1/4 inch coal. These ratios apply to both coals, even though at equal top sizes the Lower Kittanning coal has a slightly higher external surface area than the Illinois No.5 coal. The surface area ratios were computed from the mean diameters of each sieve fraction listed in Table 19 by assuming similar particle shapes for all fractions.

The majority of experiments were performed with coal samples in the 400 to 600 gram range. A limited number of experiments utilized coal samples of 100 and 1000 gram sizes. The attaining of a meaningful process mass balance was of principal concern. Equipment and apparatus were designed to accommodate these coal sample sizes under a variety of processing conditions.

The only sample preparation performed during the program, other than grinding and riffling, was drying. Unless otherwise stated, coal samples were dried overnight at 100°C under vacuum prior to processing. The principal reason for drying was attainment of uniformity in starting coals. Process chemistry was not measurably affected by typical coal sample moisture levels (2 to 10 wt.%) and process efficiency was affected only to the extent that sample moisture reduced the reactor slurry reflux temperature when the extraction solvent boiled substantially above water (organic sulfur extractions).

Table 19. Coal Particle Size Distribution

GRIND SIZE	ILLINOIS NO.5 COAL			LOWER KITTANNING COAL		
	-100 MESH	-14 MESH	-1/4 INCH	-100 MESH	-14 MESH	-1/4 INCH
Size Range(mesh)	Wt. Fraction*	Wt. Fraction*	Wt. Fraction*	Wt. Fraction*	Wt. Fraction*	Wt. Fraction*
+6			0.326±0.010			0.165±0.010
-6 +14			0.422±0.006			0.381±0.006
-14 +28		0.378±0.002	0.115±0.006		0.285±0.007	0.172±0.008
-28 +42		0.175±0.002			0.153±0.001	
-28 +48			0.061±0.004			0.112±0.004
-42 +60		0.089±0.003			0.083±0.001	
-48 +100			0.036±0.002			0.073±0.004
-60 +80		0.076±0.003			0.075±0.001	
-80 +100		0.032±0.001			0.036±0.002	
-100 +115	0.135±0.005			0.045±0.003		
-115 +150	0.110±0.001			0.065±0.003		
-150 +200	0.200±0.005			0.220±0.004		
-100 +200		0.109±0.001	0.022±0.001		0.204±0.015	0.048±0.003
-200	0.552±0.005	0.145±0.001	0.018±0.001	0.670±0.004	0.164±01015	0.049±0.003
Lost	0.003	0.006	0.002	---------	---------	---------

*Average of four samples.

3.2.3.2 Experimental Data

The experimental results are presented in the following three tabulated subsections. Because of the very large data base, the bulk of the data is in Appendix B of Volume 2, with only example tables and listings presented with the text of this section.

3.2.3.2.1 Coal Leaching - Parametric Investigation Data

Early laboratory-scale experimentation with -100 mesh coal indicated that ferric chloride was an efficient pyrite leaching agent; thus, the first bench-scale process parametric investigations were performed with this reagent. The parameters investigated were coal particle size, total iron concentration and artificial weathering. The laboratory results from sulfate ion parametric investigations (Section 3.2.2) pointed to the fact that ferric sulfate is just as efficient a pyrite leaching agent as ferric chloride. Since substitution of ferric sulfate for ferric chloride offered a number of advantages including reduced equipment corrosion, reduced system contamination (chloride is not added to coal), and higher selectivity, a change to ferric sulfate was made. However, parametric effects with either reagent proved to be similar and duplication of effort was not necessary. Deductions drawn from the ferric chloride extractions hold, in general, for ferric sulfate extractions; proven or anticipated differences are specifically mentioned in the next section.

Table 20 and Table B-1 (Appendix B of Volume 2) present the data from ferric chloride extraction of Lower Kittanning and Illinois No.5 coal samples.

Table 20 contains data on coal particle size, ferrous ion, and sulfate ion effects on pyritic sulfur removal from coals processed in batch mode. The table is divided into five parts.

TABLE 20. PYRITIC SULFUR REMOVAL FROM COAL WITH FERRIC CHLORIDE - COAL PARTICLE SIZE, SULFATE ION AND FERROUS ION EFFECTS

Part I. - Summary of Experimental Conditions.

Exp. No.	EXPERIMENTAL PARAMETERS								SULFUR RECOVERY			
	Type of Coal	Top Size	Molarities and Reagents Used	Reaction		Filtration Time (Minutes)	Washing		Toluene Reflux		Coal Drying	
				Time (Hours)	Temp. (°C)		No. of Washes	Water Temp. (°C)	Time (Minutes)	Temp. (°C)*	Temp. (°C)	Time (Hours)
A. Particle Size Effect Matrix:												
1	Illinois No. 5	100 mesh	0.99M $FeCl_3$	4	102	10	4	88	60	78	102	18
2	Illinois No. 5	100 mesh	0.99M $FeCl_3$	4	103	10	4	86	60	87	103	18
3	Illinois No. 5	14 mesh	0.99M $FeCl_3$	4	102	10	4	85	60	87	100	18
4	Illinois No. 5	14 mesh	0.99M $FeCl_3$	4	104	10	4	85	60	87	100	18
5	Illinois No. 5	1/4 inch	0.99M $FeCl_3$	4	100	15	4	93	60	83	100	18
6	Illinois No. 5	1/4 inch	0.99M $FeCl_3$	4	100	10	4	91	60	83	100	18
7	Lower Kittanning	100 mesh	0.99M $FeCl_3$	4	105	10	4	85	60	87	100	18
8	Lower Kittanning	100 mesh	0.99M $FeCl_3$	4	105	10	4	85	60	87	100	18
9	Lower Kittanning	100 mesh	0.99M $FeCl_3$	4	102	15	4	98	60	84	100	18
10	Lower Kittanning	14 mesh	0.99M $FeCl_3$	4	102	10	4	87	60	85	105	19
11	Lower Kittanning	14 mesh	0.99M $FeCl_3$	4	104	10	4	85	60	85	105	19
12	Lower Kittanning	1/4 inch	0.99M $FeCl_3$	4	98	20	4	90	60	80	103	5
13	Lower Kittanning	1/4 inch	0.99M $FeCl_3$	4	98	20	4	96	60	80	100	5
B. Sulfate and Ferrous Ion Effect Matrix:												
14	Lower Kittanning	14 mesh	1M $FeCl_3$ + 0.5M $FeCl_2$	4	103	10	4	96	60	86	103	18
15	Lower Kittanning	14 mesh	1M $FeCl_3$ + 0.5M $FeCl_2$	4	103	10	4	96	60	86	105	18
16	Lower Kittanning	14 mesh	0.63M$FeCl_3$ + 0.13M$Fe_2(SO_4)_3$	4	102	15	4	89	60	86	100	18
17	Lower Kittanning	14 mesh	0.63M$FeCl_3$ + 0.13M$Fe_2(SO_4)_3$	4	102	15	4	84	60	84	100	18
18	Lower Kittanning	14 mesh	0.98M $FeCl_3$ + 0.45M$FeSO_4$	4	102	10	4	83	60	84	105	5
19	Lower Kittanning	14 mesh	0.98M $FeCl_3$ + 0.45M$FeSO_4$	4	102	10	4	95	60	86	105	5

*Toluene - water azeotrope boils at 85°C; composition: 79.8% Toluene, 20.2% water.

TABLE 20. CONTINUED

Part II. - Process Mass Balance.

Exp. No.	WEIGHTS IN GRAMS																
	Coal in (Dry)	Processed Coal (Dry)	Toluene Distillation Residue	Coal Recovered From Filters	Solids Out-In	Reagent Solution In	Wash Water In	Toluene In	Total Liquid Charge	Liquid Out					Total Liquid Out	Liquid Out-In	Net Process Losses
										Reactor Filtrate	Combined Wash[a]	Last Wash	Toluene Distillate	Drier Traps			
A. Particle Size Effect Matrix:																	
1	433.8	435.3	8.1	3.4	13.0	1967.5	1990.2	1204.8	5162.5	1769.8	1473.1	478.5	1026.2	237.2	4984.8	-177.7	-164.7
2	379.7	369.6	8.2	2.7	0.8	1969.2	2022.6	1200.7	5192.5	1810.9	1499.5	494.8	1045.4	208.6	5059.2	-133.3	-132.5
3	441.0	440.6	3.8	3.5	6.9	1965.6	1863.1	1212.2	5040.9	1781.6	1402.3	442.2	1041.0	192.0	4859.1	-181.8	-174.9
4	430.3	413.1	3.4	5.8	-8.0	1964.8	2094.4	1242.4	5301.6	1739.4	1592.6	541.3	1093.6	123.1	5090.0	-211.6	-219.6
5	455.4	444.7	1.9	3.9	-4.9	1980.3	2077.1	1283.0	5340.4	1786.5	1566.7	438.2	1138.9	125.9	5056.2	-284.2	-289.1
6	441.4	444.7	1.5	4.7	9.5	1974.5	2012.9	1279.2	5266.6	1748.5	1602.7	451.3	1158.4	122.2	5083.1	-183.5	-174.0
7	513.2	487.8	5.5	4.1	-15.8	3938.3	2003.3	1206.5	7148.1	3752.0	1545.2	422.1	1086.9	NA	NA	NA	NA
8	511.1	487.8	5.7	4.9	-12.7	3938.8	2070.0	1263.1	7271.9	3749.9	1514.1	472.4	1121.4	NA	NA	NA	NA
9	525.8	529.9	6.7	5.8	16.6	3938.4	2044.6	1211.7	7194.7	3751.5	1529.5	503.1	1076.5	115.5	6976.1	-218.6	-202.0
10	536.2	509.7	5.7	4.7	-16.1	3955.3	1899.3	1257.3	7111.9	3831.0	1232.3	621.1	1140.9	116.2	6941.5	-170.4	-186.5
11	547.2	501.9	5.1	6.5	-33.7	3949.1	1977.2	1263.8	7190.1	3835.0	1350.3	444.8	1152.1	112.9	6895.1	-295.0	-328.7
12	503.5	493.2	3.1	4.1	- 3.1	3937.9	1975.1	1158.6	7071.6	3843.1	1430.7	493.9	1062.7	33.4	6863.8	-207.8	-210.9
13	527.8	501.4	4.0	4.4	-18.0	3938.8	1964.7	1193.7	7097.2	3852.5	1490.4	433.7	1106.6	26.4	6909.6	-187.6	-205.6
B. Sulfate and Ferrous Ion Effect Matrix:																	
14	602.1	577.4	4.4	6.9	-13.4	4121.7	1978.6	1203.8	7304.1	3973.6	1468.1	506.8	1091.4	152.8	7192.7	-111.4	-124.8
15	565.6	542.3	3.6	4.7	-15.0	4091.7	2011.4	1225.8	7328.9	3938.3	1516.2	499.1	1129.6	126.6	7209.8	-119.1	-134.1
16	503.6	476.4	3.7	4.7	-18.8	3943.2	2046.8	1160.5	7150.5	3828.5	1551.0	517.2	1079.6	115.2	7091.5	- 59.0	- 77.8
17	511.7	482.0	4.9	4.6	-20.2	3943.7	2037.6	1204.2	7185.5	3824.5	1509.0	522.3	1112.9	120.2	7088.9	- 96.6	-116.8
18	511.0	492.0	3.7	4.3	-11.0	4156.0	1953.6	1198.4	7308.0	4031.4	1421.3	518.1	1103.8	120.2	7194.8	-113.2	-124.2
19	534.5	514.0	3.0	6.4	-11.1	4158.0	2051.9	1205.4	7415.3	4021.0	1545.1	504.3	959.8	115.7	7145.9	-269.4	-280.5

NA: Not available (drier traps were not weighed, thus liquid mass balance could not be completed).

[a] Does not include filtrate of last wash.

TABLE 20. CONTINUED

Part III. - Analytical Data for Sulfur and Iron Balances

Exp. No.	ANALYTICAL DATA, WEIGHT PERCENT^b(ON DRY BASIS FOR SOLIDS)																
	Heat Content BTU/Lb	Ash	Total Sulfur In Coal	Sulfur Forms in Coal			Sulfur as Sulfate In			Sulfur In Toluene Residue	Total Iron In				Fe^{+2}		Nitrogen in Coal
				Pyritic	Sulfate	Organic	Reactor Filtrate	Combined Wash	Last Wash		Fe in Coal	Fe in Reactor Filtrate	Fe in Combined Wash	Fe in Last Wash	Reactor Filtrate	Combined Wash	
A. Particle Size Effect Matrix:																	
1	12,703	8.87	2.86	1.07	0.01	1.78	0.0648	0.0051	0.64×10^{-3}	8.5	1.18	4.780	0.547	0.57×10^{-2}	5.070	0.529	NA
2	12,629	8.64	2.83	NA	NA	NA	0.0709	0.0038	0.03×10^{-3}	9.6	1.22	5.061	0.448	0.51×10^{-2}	5.028	0.440	NA
3	12,660	9.16	2.99	1.39	0.00	1.60	0.0551	0.0031	0.03×10^{-3}	15.6	1.31	5.075	0.554	5.40×10^{-2}	5.002	0.542	NA
4	12,627	9.22	2.98	NA	NA	NA	0.0654	0.0042	0.03×10^{-3}	19.2	1.26	5.049	0.636	2.85×10^{-2}	4.960	0.619	NA
5	12,570	9.56	2.83	1.13	0.01	1.69	0.0571	0.0042	0.05×10^{-3}	30.7	1.47	5.119	0.431	9.00×10^{-2}	3.956	0.357	1.31
6	12,469	9.73	2.77	1.07	0.03	1.67	0.0554	0.0127	0.06×10^{-3}	32.1	1.52	5.118	0.510	9.60×10^{-2}	4.111	0.431	1.31
7	12,761	16.78	1.96	NA	NA	NA	0.1976	0.0185	0.61×10^{-3}	78.3	1.37	5.264	0.516	0.46×10^{-2}	3.160	0.300	NA
8	12,262?	16.86	1.81	1.38	0.01	0.42	0.2040	0.0156	1.0×10^{-3}	84.8	1.31	5.298	0.500	13.00×10^{-2}	3.089	0.293	NA
9	12,701	16.12	1.87	1.22	0.03	0.62	0.1879	0.0171	0.50×10^{-3}	80.5	1.29	5.224	0.390	0.54×10^{-2}	2.932	0.265	NA
10	12,611	17.40	2.08	1.57	0.01	0.50	0.1884	0.0157	0.77×10^{-3}	82.9	1.50	5.344	0.458	0.42×10^{-2}	2.861	0.259	NA
11	12,798	16.86	2.17	NA	NA	NA	0.1931	0.0142	0.05×10^{-3}	84.2	1.50	5.288	0.389	0.72×10^{-2}	2.898	0.225	NA
12	12,567	18.13	2.90	2.44	0.02	0.44	0.1101	0.0050	0.98×10^{-3}	83.6	2.22	5.173	0.213	0.52×10^{-2}	1.811	0.086	1.09
13	12,724	17.65	3.09	2.64	0.02	0.43	0.1274	0.0043	0.94×10^{-3}	80.6	2.20	5.210	0.232	0.29×10^{-2}	1.889	0.095	1.09
B. Sulfate and Ferrous Ion Effect Matrix:																	
14	12,996	16.02	2.45	1.87	0.00	0.60	0.1522	0.0092	0.38×10^{-3}	86.2	1.85	7.397	0.708	0.87×10^{-3}	4.796	0.460	NA
15	12,929	16.03	2.42	1.87	0.00	0.57	0.1606	0.0134	0.32×10^{-3}	83.7	1.79	7.535	0.635	0.61×10^{-3}	4.850	0.418	NA
16	12,764	16.99	2.42	1.66	0.02	0.74	1.3499	0.0971	1.34×10^{-3}	84.7	1.63	4.540	0.356	0.30×10^{-3}	2.608	0.200	NA
17	13,052	15.65	2.04	1.39	0.02	0.63	1.3385	0.1001	1.09×10^{-3}	83.5	1.49	4.842	0.354	0.27×10^{-3}	2.680	0.203	NA
18	12,777	16.93	2.69	1.99	0.06	0.64	1.3025	0.0995	0.93×10^{-3}	86.1	1.99	6.952	0.543	0.40×10^{-3}	4.121	0.322	NA
19	12,790	15.75	2.42	1.76	0.08	0.57	1.4988	0.1147	Lost	80.3	1.85	7.310	0.539	Lost	4.556	0.341	NA
Untreated Coals (11 Sample Averages)																	
Illinois No. 5	12,700 ± 73	11.34 ± 0.31	3.53 ± 0.07	1.56 ± 0.12	0.07 ± 0.02	1.96 ± 0.17					1.53 (3 sample avg)						1.35 ± 0.03
Lower Kittanning	12,319 ± 109	19.72 ± 0.60	4.22 ± 0.12	3.59 ± 0.17	0.06 ± 0.03	0.67 ± 0.12					3.15 ± 0.10 (3 sample avg)						1.16 ± 0.07

NA: Not available (sulfur forms and nitrogen determinations were not performed).

^{b}Except for heat content

TABLE 20. CONTINUED

Part IV. - Sulfur Balances and Sulfur Removal Estimates.

	SULFUR BALANCE, GRAMS																				
	Sulfur In			Sulfur Out							Estimated Pyrite Removal From^d						Produced^e Sulfate		Produced Elemental Sulfur		
Exp. No.	From Coal	From Reagents	Total in	In Processed Coal	In Reactor Filtrate	In Combined Wash	In Last Wash	In Toluene Residue	Sulfur Out-In^c	Pyritic Sulfur In	Δ Total Sulfur In Coal		Δ Sulfur Forms In Coal		Produced S_n + SO_4^{-2}		Grams (as sulfur)	m Moles	Grams	mMoles	SO_4/S_n
											Grams	%	Grams	%	Grams	%					
A. Particle Size Effect Matrix:																					
1	15.31	0	15.31	12.45	1.15	0.08	0.01	0.69	-0.94	6.77	2.86	42.3	2.11	31.2	1.92	28.4	1.23	38.4	0.69	21.6	1.78
2	13.40	0	13.40	10.46	1.28	0.06	0.01	0.79	-0.81	5.92	2.94	49.7	NA	NA	2.13	36.0	1.34	41.9	0.79	24.7	1.70
3	15.57	0	15.57	13.17	0.98	0.04	0.01	0.59	-0.79	6.88	2.39	34.8	0.76	11.0	1.61	23.4	1.02	31.9	0.59	18.4	1.73
4	15.19	0	15.19	12.31	1.14	0.07	0.01	0.65	-1.02	6.71	2.88	42.9	NA	NA	1.86	27.7	1.21	37.8	0.65	20.3	1.86
5	16.08	0	16.08	12.59	1.02	0.07	0.01	0.58	-1.82	7.10	3.49	49.1	2.08	29.3	1.67	23.5	1.09	34.1	0.58	18.1	1.88
6	15.58	0	15.58	12.32	0.97	0.20	0.01	0.48	-1.61	6.89	3.26	47.3	2.13	30.9	1.65	23.9	1.17	36.6	0.48	15.0	2.44
7	21.66	0	21.66	9.56	7.41	0.29	0.01	4.31	-0.09	18.42	12.10	65.7	NA	NA	12.01	65.2	7.70	240.6	4.31	134.7	1.79
8	21.57	0	21.57	8.83	7.65	0.24	0.01	4.83	-0.02	18.35	12.74	69.4	11.62	63.3	12.72	69.3	7.89	246.6	4.83	150.9	1.63
9	22.19	0	22.19	9.91	7.05	0.26	0.01	5.39	+0.42	18.88	12.28	65.0	12.41	65.7	12.70	67.3	7.31	228.4	5.39	168.4	1.36
10	22.63	0	22.63	10.60	7.22	0.19	0.01	4.73	+0.11	19.25	12.03	62.5	11.25	58.4	12.14	63.1	7.41	231.6	4.73	147.8	1.57
11	23.09	0	23.09	10.89	7.41	0.19	0.01	4.29	-0.31	19.64	12.20	62.1	NA	NA	11.89	60.5	7.60	237.5	4.29	134.1	1.77
12	21.25	0	21.25	14.30	4.23	0.07	0.01	2.59	-0.06	18.08	6.94	38.4	6.04	33.4	6.89	38.1	4.30	134.4	2.59	80.9	1.66
13	22.27	0	22.27	15.49	4.91	0.06	0.01	3.22	+1.41	18.95	6.78	35.8	5.71	30.1	8.19	43.2	4.97	155.3	3.22	100.6	1.54
B. Sulfate and Ferrous Ion Effect Matrix:																					
14	25.41	0	25.41	14.15	6.05	0.14	0.01	3.79	-1.28	21.62	11.26	52.1	10.82	50.0	9.98	46.2	6.19	193.4	3.79	118.4	1.63
15	23.87	0	23.87	13.12	6.32	0.20	0.01	3.01	-1.22	20.30	10.75	53.0	10.16	50.0	9.53	46.9	6.52	203.8	3.01	94.1	2.17
16	21.25	49.72*	70.97	11.53	51.68*	1.51	0.01	3.13	-3.12	18.08	9.72	53.8	10.17	56.3	6.60	36.5	3.47	108.4	3.13	97.8	1.11
17	21.59	49.72*	71.31	9.83	51.19*	1.51	0.01	4.09	-4.69	18.37	11.76	64.0	11.67	63.5	7.07	38.5	2.98	93.1	4.09	127.8	0.73
18	21.56	59.58*	81.14	13.23	52.51*	1.41	0.01	3.19	-10.80	18.34	8.33	45.4	8.55	46.6	-2.47	--	-5.66	--	3.19	99.7	- -
19	22.56	59.61*	82.17	12.44	60.27*	1.77	<0.01	2.41	-5.28	19.19	10.12	52.7	10.14	52.8	4.84	25.2	2.43	75.9	2.41	75.3	1.01

[c] Difference between sulfur recovered and sulfur removed from coal according to Eschka analyses of feed and processed coal samples.

[d] Three methods of computing sulfur removal are indicated.

[e] Difference between sulfate collected and that added to the reactor.

*Sulfate analysis precision estimated to be ±3% giving a pyrite removal estimate about ±20%.

TABLE 20. CONTINUED

Part V. - Iron Mass Balance Data.

Exp. No.	FERRIC AND FERROUS ION BALANCE, GRAMS												Moles Fe^{+3} Used[h]	Theoretical Moles Fe^{+3} Used[i]	Percent XS Fe^{+3} Used[j]
	Fe^{+3} In (Reagents)	Fe^{+3} Out			Fe^{+3} Used In-Out	Fe^{+2} In			Fe^{+2} Out		Fe^{+2} Produced Out-In	Unaccounted Fe^{+3} g[g]			
		Reactor Filtrate	Combined Wash	Total Out		Fe Coal[f]	Reagents	Total In	Reactor Filtrate	Wash Filtrate					
A. Particle Size Effect Matrix:															
1	108.8	0	0.3	0.3	108.5	1.5	0	1.5	89.7	7.6	96.1	-12.4	1.72	0.29	493
2	108.9	0.6	0.1	0.7	108.2	1.3	0	1.3	91.1	6.6	96.5	-11.7	1.73	0.32	441
3	108.7	1.3	0.2	1.5	107.2	1.0	0	1.0	89.1	7.8	96.1	-11.1	1.72	0.24	616
4	108.6	1.5	0.3	1.8	106.8	1.4	0	1.4	86.3	10.1	95.2	-11.6	1.70	0.28	507
5	109.5	20.8	1.2	22.0	87.5	0.4	0	0.4	70.7	6.0	76.2	-11.3	1.37	0.26	427
6	109.2	17.6	1.3	18.9	90.3	0.0	0	0.0	71.9	7.3	79.2	-11.1	1.41	0.27	422
7	217.8	78.9	3.3	82.2	6	9.4	0	9.4	118.6	4.6	113.8	-21.8	2.04	1.82	12
8	217.8	82.8	3.1	85.9		9.7	0	9.7	115.8	5.0	111.1	-20.8	1.99	1.88	5
9	217.8	86.0	1.9	87.		9.6	0	9.6	110.0	4.1	104.5	-25.4	1.87	1.77	6
10	218.7	95.1	2.5	97.	[illegible]	9.2	0	9.2	109.5	3.2	103.5	-17.6	1.85	1.77	5
11	218.4	91.7	2.2	93.		9.7	0	9.7	111.1	3.1	104.5	-20.0	1.87	1.80	4
12	217.7	129.2	1.8	131.0		4.9	0	4.9	69.6	1.2	65.9	-20.8	1.18	1.02	16
13	217.8	127.9	2.0	129.9	.9	5.6	0	5.6	72.8	1.4	68.6	-19.3	1.23	1.19	3
B. Sulfate and Ferrous Ion Effect Matrix:															
14	230.2	103.3	3.6	106.9	123.3	8.1	115.1	123.2	190.6	6.8	74.2	-49.1		1.47	--
15	229.5	105.8	3.3	109.1	119.4	8.1	114.3	122.4	191.0	6.3	74.9	-44.9	1.34	1.52	--
16	196.0	74.0	2.4	76.4	119.6	8.0	0	8.0	99.8	3.1	94.9	-24.7	1.70	0.86	98
17	196.0	82.7	2.2	84.9	111.1	8.9	0	8.9	102.5	3.1	96.7	-14.4	1.73	.7[illegible]	122
18	227.5	114.1	3.1	117.2	110.2	6.3	104.5	110.8	166.1	4.6	59.9	-50.3	1.07	--	--
19	227.6	110.7	3.1	113.8	113.8	7.3	104.5	111.8	183.1	5.3	76.6	-37.2	1.37	[illegible]	125

Exp. No.	TOTAL IRON BALANCE, GRAMS								
	Fe In			Fe Out					Δ Fe Out-In
	From Coal	From Reagents	Total In	In Reactor Filtrate	In Combined Wash	In Last Wash	In Processed Coal	Total Out	
A. Particle Size Effect Matrix:									
1	6.5	108.8	115.3	84.6	8.1	0.03	5.1	97.8	-17.5
2	5.8	108.9	114.7	91.6	6.7	0.03	4.5	102.9	-11.8
3	6.7	108.7	115.4	90.4	7.8	0.2	5.8	104.2	-11.2
4	6.6	108.6	115.2	87.8	10.1	0.2	5.2	103.3	-11.9
5	7.0	109.5	116.5	91.5	6.8	0.4	6.5	105.2	-11.3
6	6.8	109.2	116.0	89.5	8.2	0.4	6.8	104.9	-11.1
7	16.2	217.8	234.0	197.5	8.0	<0.03	6.7	212.2	-21.8
8	16.1	217.8	233.9	198.7	7.6	0.6	6.4	213.3	-20.6
9	16.6	217.8	234.4	196.0	6.0	0.03	6.9	208.9	-25.5
10	16.9	218.7	235.6	204.7	5.6	0.03	7.7	218.0	-17.6
11	17.2	218.4	235.6	202.8	5.3	0.03	7.5	215.6	-20.0
12	15.9	217.7	233.6	198.8	3.0	0.03	10.9	212.7	-20.9
13	16.6	217.8	234.4	200.7	3.5	0.03	11.0	215.2	-19.2
B. Sulfate and Ferrous Ion Effect Matrix:									
14	18.9	345.3	364.2	293.9	10.4	0.03	10.7	315.0	-49.2
15	17.6	342.6	360.6	296.8	9.6	0.03	9.7	316.1	-44.5
16	15.8	196.0	211.8	173.8	5.5	0.03	7.8	187.1	-24.7
17	16.1	196.0	212.1	185.2	5.3	0.03	7.2	197.7	-14.4
18	16.1	332.0	348.1	280.3	7.7	0.03	9.8	297.8	-50.3
19	16.8	332.1	348.9	293.9	8.3	0.03	9.5	311.7	-37.2

[f] Assumes that Fe removed from coal was of +2 valence.
[g] The difference between "Fe^{+3} used" and Fe^{+2} produced.
[h] Based on "Fe^{+2} produced".
[i] Based on "Collected Elemental Sulfur and Sulfate".
[j] Excess of calculated "theoretical usage".

Part I shows the experimental conditions under which the coal samples were processed. Approximately one pound coal samples were mixed with preheated ferric chloride solution in a 5 liter, heated reactor equipped with stirrer and reflux condenser. Approximately 1M ferric ion solutions of pure ferric chloride, or ferric chloride plus ferric sulfate, were used. The reagent to coal weight ratio was four for the Illinois No.5 coal and eight for the Lower Kittanning coal (the latter coal has approximately twice the pyrite concentration of the former).

After 4 hours extraction, at reflux temperatures, the hot slurry was vacuum filtered, washed four times with hot water (the last wash water collected and analyzed separately), and the wet coal was transferred to another reactor for extraction with toluene. Toluene extraction serves as a means of elemental sulfur recovery in all the experiments performed in this program.

After 1 hour of extraction the slurry was filtered and the coal (wet with toluene) was rinsed with additional toluene and vacuum dried at approximately 100°C for the indicated time (usually overnight). The toluene filtrate contained the elemental sulfur and a small amount of dissolved coal both of which were separated from toluene by distillation.

Part II of Table 20 indicates the process mass balance from each experiment, which in general shows good recovery of input materials.

Part III presents analytical data for sulfur and iron balances. As indicated in Figure 7, all solids and solutions, including traps, were analyzed for pertinent data. In most cases the solid samples were examined at Commercial Testing and Engineering Co. for short proximate analyses, sulfur forms, nitrogen, and iron by the usual ASTM methods. Solutions were analyzed by TRW.

Parts IV of this table presents the sulfur mass balance for each experiment and the estimated pyrite removal computed by three methods, each of which utilized independent data. The column titled "Sulfur Out-In" indicates the difference between the sulfur content of the processed coal plus the sulfur recovered as sulfate and elemental sulfur (sulfur out) and the sulfur input to the system with the starting coal and reagents (in the cases where ferric or ferrous sulfate was added). Adequate sulfur balances were obtained in Experiments 1 through 15, but not in Experiments 16 through 19, where iron sulfate was added to the system. The reason is that the sulfate produced from the oxidation of the coal pyrite represented a small fraction of the total sulfate in the system; thus, a small error in sulfate analysis resulted in large errors in the "Produced Sulfate" entry. In later experiments where ferric sulfate was the reagent, the sulfate produced was indirectly determined from elemental sulfur and ferrous ion production (see Table B-11 in Appendix B of Volume 2 for method of computation). The last column of Part IV (Table 20) shows the sulfate sulfur to elemental sulfur ratio as computed from the recovered amounts of sulfate and elemental sulffur produced from the reacted pyrite. This ratio appears to be approximately 1.8 for Illinois No.5 coal and about 1.6 for Lower Kittanning coal. Subsequent bench-scale data indicated the ratio to be closer to 1.5 for both coals.

The "estimated pyrite removal" by the three independent methods of computation are in substantial agreement in the case of Lower Kittanning coal but are in disagreement for the Illinois No.5 coal. This disagreement could not be explained from the available data. Additional work in analysis of processed Illinois No.5 coals is required in order to definitely identify the correct set of sulfur removal values for this coal. Because of the relative reliability of Eschka coal analysis, sulfur removal values based on total sulfur analysis of feed and processed coal samples are assumed as the correct ones for this coal.

Sulfur removal was computed as follows: the grams of total sulfur in the processed coal (adjusted for losses when significant) was subtracted from the grams of total sulfur present in the starting coal samples, and the difference was divided by the pyritic sulfur content of the starting coal and multiplied by 100. This value for each experiment is in the column titled "Estimated Pyrite Removal from Total Sulfur."

A similar computation was performed with the weights of pyritic sulfur present in the starting and processed coal (sulfur form analyses).

These values are listed in the column labelled "Estimated Pyrite Removal from Sulfur Forms". Finally, the weight of sulfur found as elemental and as sulfate in the various solutions (spent reagent, spent wash water, spent toluene and traps) in excess of sulfate input to the system was divided by the pyritic sulfur input and multiplied by 100 to furnish the entries of the column titled "Estimated Pyrite Removal from Produced Sulfur and Sulfate."

Part V of Table 20 presents data on iron species mass balance (total iron, ferric,and ferrous ions), shows the ferrous ion produced from the oxidation of pyrite,and indicates (last column) the computed percent excess usage of ferric ion above that theoretically required for the oxidation of the pyrite removed from each coal sample. The theoretical requirement for ferric ion consumption was computed on the bases of stoichiometry; the molar amount of ferric ion consumed is equivalent to the sum of the net moles of sulfate and elemental sulfur produced multiplied by 7 and 1, respectively, as dictated by the following process chemistry:

$$Fe_2(SO_4)_3 + FeS_2 \longrightarrow 3\ FeSO_4 + 2S^0$$

$$7Fe_2(SO_4)_3 + 8H_2O + FeS_2 \longrightarrow 15\ FeSO_4 + 8H_2SO_4$$

Within experimental uncertainty, the ferric chloride reagent reacted selectively with the pyrite of Lower Kittanning coals. This was not the case with Illinois No.5 coal which experienced 400 to 600 percent excess usage of ferric ion. The assumption is that the excess usage is due to coal oxidation, even though the latter was still too small to definitely detect from heat content determination of the processed coals (see Part III of this table). The excess usage of ferric ion has been substantially curtailed through substitution of ferric sulfate for ferric chloride.

The data in Table 20 reveals that coal particle size and ferrous ion concentration in the leacher have a pronounced effect on pyritic sulfur removal from Lower Kittanning coal. Sulfate ion does not appear to affect sulfur removal. Details on the effects of all investigated parameters on process efficiency are discussed in subsection 3.2.3.3 of this report (Discussion of Results).

Data on the effects of artificial weathering of coal were experimentally determined and are presented in Table B-1 of Appendix B, Volume 2. Weathering was simulated by refluxing coal samples in water for four hours with air continuously bubbling through the system. The purpose of this pre-treatment was to determine the effect of coal weathering on the extent of pyrite removal and on excess ferric ion consumption. Within experimental uncertainty neither quantity was influenced by the pre-treatment.

3.2.3.2.2 Coal Leaching - Reaction Rate Data

After trends of parameter variations on the process had been established, the important reaction and processing parameters were identified for investigation of their quantitative effect on pyrite leaching rates. The reaction parameters selected were coal particle size, ferric ion to total iron ratio, total iron concentration, and temperature. Four processing modes were also investigated: continuous-concurrent leaching, continuous counter-concurrent leaching, multi-batch counter-current leaching and continuous-concurrent followed by batch leaching. The generated data were analyzed and a rate expression was developed which accurately describes pyritic sulfur leaching from -100 mesh or finer Lower Kittanning coal as a function of time, Fe^{+3} to total Fe ratio, and total iron concentration at constant temperature. Finally, a few experiments probing process improvements were conducted with very promising results. These included elemental sulfur recovery prior to coal washing, pyrite leaching under pressure (higher than normal reflux temperatures), and pyrite leaching with concurrent reagent regeneration.

Table B-3 of Appendix B, Volume 2, lists the conditions under which the leacher was operated in each of these experiments (Nos.42 through 64). All other process unit operations (filtration, washing, sulfur recovery, drying) were performed as previously described with two exceptions: in both Experiments 47 and 48 elemental sulfur recovery preceded coal washing.

Part of the data generated from these experiments is grouped in seven tables (B-4 through B-10) in Appendix B, within which results from each experiment are separately presented. Each table groups experiments covering one major reaction or process parameter variation.

The complete raw and reduced data are too voluminous to be included in this report. A computer printout of results from each experiment (described below) was generated and consists of six tables, some of which are several pages long. However, the selected table for inclusion in this report summarizes sufficient data for clear understanding of the results which were obtained.

The computer program written for the pyritic sulfur leaching process (except reagent regeneration) required the following input:

- Coal charge weight and analysis (short proximate and sulfur forms).
- Reagent charge weight and its total iron and ferrous ion composition.
- Rates (continuous) or frequency (multi-batch) of all reagent exchanges during extraction.
- Weight and composition (iron) of all samples taken during extraction (including weight fraction of solids withdrawn with sample).
- Weight of wet coal after extraction.
- Input and output weights from filtrations, washes, elemental sulfur recovery, and drying operations (including liquids and solids retained on filter papers).
- Composition of processed coal (short proximate analysis and sulfur forms).

The output consisted of the following tables:

- Complete listing of both mass and composition of reactor charges and withdrawals.
- Complete reactor mass balance at the end of each sampling interval (usually 15 minutes). This includes weights of coal, liquid, pyrite dissolved, sulfate produced, non-pyritic ash dissolved, total iron, and ferrous ion in solution.
- Reaction rate data table showing instantaneous and average pyritic sulfur removal rates based on available residual and initial pyritic sulfur concentration.
- Summary of reaction rate data table (included in this report and described in detail below).
- Individual unit operation mass balance table.
- Overall process mass balance table for solids, liquids, sulfur, and iron.

Table 21 below presents data from one reaction rate experiment (No.45). This table is presented here for illustrative purposes only. The type of data contained in the table is identical to that presented for all reaction rate experiments in Appendix B, and the explanation and discussion which follows applies to all of them.

Table 21. CONTINUOUS EXTRACTION OF -14 MESH LOWER KITTANNING COAL WITH FERRIC SULFATE AT 102°C.

SUMMARY OF REACTION DATA FOR SO4/S= 1.500

Experiment 45.

MIN FROM START	FE+2/FE WT. RATIO	COAL WT. FREE OF S(ELEM)	PYRITE REMOVED PCT OF INIT	CUMULATIVE RATE PCT/HR	CALCULATED COAL ANALYSES STEP-BY-STEP TOTAL S WT-PCT	PYR. S WT-PCT	ORG. S WT-PCT	SO4 S WT-PCT	ASH WT-PCT	HT CONTENT BTU/LB
15	.2459	1000.79	16.80	67.21	3.770	3.029	.680	.061	19.136	12432
30	.2951	996.41	21.99	43.98	3.596	2.853	.683	.061	18.898	12476
45	.3320	992.65	26.44	35.25	3.447	2.700	.685	.061	18.694	12514
60	.3559	990.09	29.46	29.46	3.344	2.596	.687	.062	18.553	12540
75	.3659	987.66	32.33	25.87	3.247	2.497	.689	.062	18.419	12565
90	.3718	985.33	35.10	23.40	3.152	2.400	.690	.062	18.290	12589
105	.3759	983.33	37.46	21.40	3.071	2.318	.692	.062	18.179	12610
120	.3790	981.47	39.66	19.83	2.995	2.240	.693	.062	18.074	12629
135	.3790	979.70	41.75	18.56	2.923	2.166	.694	.062	17.975	12648
150	.3769	978.09	43.66	17.46	2.857	2.099	.695	.062	17.885	12665
165	.3751	976.51	45.53	16.56	2.791	2.033	.696	.062	17.795	12681
180	.3710	975.17	47.11	15.70	2.736	1.976	.697	.062	17.720	12695
195	.3651	973.74	48.80	15.01	2.677	1.916	.698	.063	17.639	12710
210	.3569	971.90	50.98	14.56	2.600	1.838	.700	.063	17.534	12730
225	.3459	970.67	52.43	13.98	2.549	1.786	.701	.063	17.463	12743
240	.3331	969.84	53.42	13.35	2.514	1.750	.701	.063	17.415	12752
255	.3210	968.94	54.48	12.82	2.476	1.712	.702	.063	17.364	12762
270	.3090	967.87	55.75	12.39	2.432	1.666	.703	.063	17.302	12773
285	.2969	966.94	56.85	11.97	2.392	1.626	.703	.063	17.249	12783
300	.2859	966.25	57.67	11.53	2.363	1.596	.704	.063	17.209	12790
315	.2751	965.59	58.44	11.13	2.336	1.568	.704	.063	17.171	12797
330	.2641	964.96	59.19	10.76	2.309	1.541	.705	.063	17.134	12804
345	.2569	964.10	60.21	10.47	2.272	1.504	.705	.063	17.084	12814
360	.2520	962.92	61.60	10.27	2.223	1.453	.706	.063	17.016	12826
FROM FINAL COAL ANALYSIS			65.77		2.200	1.300	.760	.140	16.810	12836

The entries in Table 21, except for those in the last row, represent predicted reactor slurry composition and pyrite removal rates at the time of each reactor sampling as listed in the first column. The values in the second through ninth columns are calculated from initial coal sample and reagent composition data, iron species analyses at each of the indicated intervals, and iron species composition of added and withdrawn reagent. Stoichiometric reaction of pyrite with ferric ion is assumed (no side reactions) and the pyritic sulfur removed is partitioned between sulfate and elemental sulfur at the ratio of 1.5 to 1. Both assumptions have been proven valid for Lower Kittanning coal extractions.

The entries under the last two columns required, in addition to the above input data, the heat and ash content of the processed coal. The last row of the table indicates the final composition of the processed coal and the extent of pyritic sulfur removal as determined by direct analysis of the before-and-after processing coal sample. The agreement between predicted and direct analysis values is very good. Such good agreement was not the case with every experiment performed, but with justifiable exceptions (simultaneous coal leaching-reagent regeneration, ferric ion consumption by coal matrix), the agreement has been adequate for utilizing this form of data generation and reduction to develop rate expressions for pilot and commercial plant design.

Table 22 summarizes the predicted and analyzed (sulfur forms) processed coal composition and pyrite removal obtained from the reaction rate experiments (Nos.42 through 64). The purpose of this table is to indicate the degree of reliability of calculated vs analytical determinations of sulfur compositions and removals. Detailed description of experimental processing parameters are presented in Table B-3, Appendix B, and should be referred to for experiments in Table 22 indicating similar processing conditions. The agreement between predicted and analyzed values is very good in more than 70% of the experiments. When considering the number of iron analyses performed in each experiment, ranging from 50 to 200 depending on experiment duration, the observed 1 to 6% difference in the sulfur removal values is remarkable. Question marks next to a few of the predicted sulfur removal values indicate uncertainty. It is possible that the analyzed value rather than the predicted value is in error; however,

TABLE 22. PREDICTED AND ANALYZED PRODUCT COAL COMPOSITION AND PERCENT PYRITIC SULFUR REMOVAL

LOWER KITTANNING COALS

Experiment No.	Coal Particle Size	Extraction Temp. °C	Extraction Time Hrs.	Processed Coal Composition							Pyritic Sulfur Removal (% of initial)
				Source of Composition Values	Heat Content (BTU/LB)	Ash (Wt.%)	Tot. S (Wt. %)	Org. S (Wt. %)	SO_4 S (Wt. %)	Pyr. S (Wt.%)	
43	-1/4 inch	102	4	Predicted* Analyzed**	12450 12384	19.12 19.00	3.24 3.09	0.68 0.45	0.06 0.32	2.49 2.32	31.80 36.74
44	-1/4 inch	102	6	Predicted Analyzed	12598 12126	18.31 18.29	2.86 3.00	0.69 0.69	0.06 0.22	2.11 2.09	43.00 43.62
45	-14 mesh	102	6	Predicted Analyzed	12826 12836	17.02 16.81	2.22 2.20	0.71 0.76	0.06 0.14	1.45 1.30	61.60 65.77
46	-200 mesh	102	12.5	Predicted Analyzed	12802 12253	17.39 17.21	1.38 1.60	0.71 0.92	0.06 0.29	0.61 0.39	83.93 89.75
47	-100 mesh	102	4	Predicted Analyzed	12580 12707	18.33 17.84	3.23 3.07	0.69 0.78	0.06 0.15	2.48 2.14	32.76? 42.57
48	-100 mesh	102	4	Predicted Analyzed	12638 12710	18.08 17.78	2.77 2.80	0.69 0.90	0.06 0.14	2.02 1.76	45.78 52.94
49	-100 mesh	102	12.5	Predicted Analyzed	12375 12736	16.87 16.60	1.57 1.66	0.71 0.90	0.06 0.22	0.79 0.54	79.16 85.90
50	-100 mesh	102	12.7	Predicted Analyzed	12922 12744	16.69 16.64	1.15 1.43	0.72 0.86	0.06 0.25	0.37 0.32	90.43 91.65
51	-100 mesh	85	12.0	Predicted Analyzed	12888 12142	16.85 16.71	1.34 1.33	0.71 0.73	0.06 0.18	0.56 0.42	85.29 89.03
52	-100 mesh	70	12.0	Predicted Analyzed	12799 12836	17.26 17.21	1.96 1.91	0.71 0.66	0.06 0.11	1.19 1.14	68.55 69.88
53	-100 mesh	85 to 102	15.0	Predicted Analyzed	13064 13258	15.62 14.26	1.74 1.26	0.72 0.93	0.07 0.21	0.96 0.12	75.27? 96.96
54	-100 mesh	102	12.5	Predicted Analyzed	13042 12937	15.75 14.76	1.79 1.44	0.72 0.79	0.06 0.26	1.00 0.39	73.95? 90.05
55	-100 mesh	102	12.5	Predicted Analyzed	12898 13069	16.75 16.33	1.48 1.50	0.71 0.95	0.06 0.24	0.70 0.31	81.64? 91.95
56	-100 mesh	102	12.4	Predicted Analyzed	13175 12742	15.00 14.58	1.38 1.41	0.73 0.84	0.06 0.24	0.59 0.33	84.99 91.60
57	-100 mesh	102	12.4	Predicted Analyzed	12942 12887	16.48 16.28	1.45 1.61	0.72 0.85	0.06 0.26	0.67 0.50	82.52 [illegible]
58	-100 mesh	102	12.5	Predicted Analyzed	13058 12887	15.73 15.49	1.47 1.75	0.72 0.83	0.07 0.40	0.69 0.52	82.25 86.60
59	-100 mesh	102	12.5	Predicted Analyzed	12765 12382	17.30 16.25	2.60 2.24	0.70 0.78	0.06 0.33	1.84 1.13	50.98? 70.49
60	-100 mesh	95 to 102	6	Predicted Analyzed	12856 12895	17.01 16.92	1.53 1.68	0.71 0.77	0.06 0.25	0.75 0.66	80.25 82.68
61	-1/4 in +10 mesh	120	4	Predicted Analyzed	11523 11446	22.67 22.59	4.44 4.23	0.37 0.22	0.14 0.12	3.92 3.89	18.52 19.39
62	-1/4 in + [illegible] mesh	140	4	Predicted Analyzed	11406 11390	23.45 23.31	4.25 5.07	0.37 0.46	0.14 0.81	3.92 3.80	17.90 20.55
63	-100 Mesh	130	4	Predicted Analyzed	12593 9585	18.26 17.28	3.19 2.85	0.69 0.69	0.06 1.48	2.44 0.68	33.93? 81.00
64	-100 mesh	130	2	Predicted Analyzed	12353 11815	19.57 17.48	4.06 2.36	0.67 0.83	0.06 0.97	3.22 0.56	8.04 84.00
ILLINOIS NO. 5 COAL											
42	-1/4 inch	102	4	Predicted Analyzed	13110 12605	8.56 9.69	2.61 3.57	2.04 1.95	0.07 0.70	0.50 0.92	69.23 42.42

*Predicted from iron species (ferrous and total) analyses

**From feed and product coal analyses for pyrite consideration of the other values in coal composition indicate that the removal value based on pyritic sulfur analysis is most likely the correct one. Most sources of error in the predicted values are probably errors in analysis of starting solutions.

The observed discrepancy between "predicted and analyzed" values in Experiment 64 was expected due to the fact that the produced ferrous ion (basis for predicted compositions and removals) from the oxidation of pyrite was simultaneously regenerated to ferric ion by the oxygen added to the system. Ferrous ion analyses during the course of this run would therefore not follow the actual progress of coal desulfurization. The differences in composition and removal values seen in Experiment 63 were not expected, but are due to the experimental observation that coal leaching at temperatures above 120°C (under pressure) gives rise to a form of ferrous sulfate which remains partially on the coal during reaction. Thus, the measured ferrous ion in the reactor solution is much lower than that corresponding to the extent of pyrite oxidation.

The iron content of the processed coals from Experiments 62 and 63 was substantially higher than that corresponding to the residual pyrite and indicated the presence of both iron sulfate and oxide on the coal. Thus, the product coal's heat content value was reduced, ash content was high, and total sulfur content was higher than expected (from pyritic sulfur analyses) by an amount equal to the residual sulfate. A modified coal washing procedure removed the residual sulfate from the processed coal, reduced the iron content to the expected value, reduced the residual total sulfur content and improved pyritic sulfur removal by more than 10%. These experiments are discussed in more detail in Section 3.2.3.3.9.

Finally, the larger "predicted" pyritic sulfur removal value for the Illinois No.5 coal (final experiment) was expected since ferric sulfate slightly oxidizes the organic matrix of this coal. The inability to accurately follow pyritic sulfur removal rates from iron analysis of Illinois No.5 coal was the primary reason why rate data generation was restricted to Lower Kittanning coal. Direct rate determination with the Illinois No.5 coal would require complete coal processing for periods varying from 30 minutes to 12 hours (with frequent sampling). Therefore, it was decided to thoroughly define the Lower Kittanning coal's ferric sulfate leaching system and use the generated data in conjunction with a few experiments with the Illinois coal to indirectly define the latter's chemical desulfurization characteristics. The generated data with this coal are presented in Table 20 (Subsection 3.2.3.2.1) and Tables B-1, B-2 and B-4, Appendix B of Volume 2. The conclusion was drawn that rate expressions developed for Lower Kittanning coal should apply to Illinois No.5 coal (Subsection 3.2.3.3.7).

3.2.3.2.3 Reagent Regeneration Data

Ferric sulfate regeneration data is summarized in Table 23. The first column of this table lists the experiment numbers. The second and third columns indicate the composition of the starting solution (spent ferric sulfate reagent). Reagent composition as a function of regeneration time is illustrated in the central group of columns of the table. The final two columns provide an indication of the average reagent composition change with time(represented by the slope of a Fe/Fe^{+2} vs time curve for the following two reaction intervals: from 20 minutes to end of reaction and from 60 minutes to end of reaction. The data indicated a second order dependence on ferrous ion (Subsection 3.2.3.3.8); thus, the Fe/Fe^{+2} vs time curve)for each run should be linear in the absence of geometric effects. The values of the entries in the last two columns of Table 23 were obtained by least square treatment of the data for each experiment and each of the indicated time intervals. The constancy of the slope was tested on reaction time intervals starting at 20 and 60 minutes after regeneration reaction initiation. The time interval of 0 to 20 minutes was not included in order to avoid data distortion from geometric effects present in a number of experiments during the high initial regeneration rates (for details refer to Discussion of Results section).

The experiments included in this table represent the total bench-scale effort involving regeneration parametric studies which were performed as a separate unit operation. Parameters and ranges of parameters investigated are listed below:

- Oxidant - air and oxygen
- Pressure - 30, 100 and 150 psig
- Temperature - 70, 100, 120 and 160°C

TABLE 23. REAGENT REGENERATION DATA SUMMARY

Exp. No.	Starting Solution		Fe/Fe^{+2} ratio in samples during the experiment														Slope $\Delta(Fe/Fe^{+2})/min$	
	% Fe	Fe/Fe^{+2}	10 min	20 min	30 min	40 min	50 min	60 min	75 min	90 min	105 min	120 min	135 min	150 min	165 min	180 min	20 min to end of Reaction	60 min to end of Reaction
R 1	4.87	3.57	3.83	4.02	4.27	4.50	4.67	4.98	5.26	5.56	5.85	6.10	6.41	6.62	6.90	7.14	.0142	.0128
R 2	4.83	2.58	2.89	2.95	2.99	3.04	3.06	3.09	3.12	3.19	3.26	3.32	3.34	(3.15)	3.46	3.56	.0041	.0043
R 3	4.35	3.33	3.76	3.86	4.03	4.27	4.46	4.74	4.95	5.24	5.68	6.13	-	-	-	-	.0220	.0234
R 4	4.63	3.39	5.68	7.19	4.33	4.83	4.52	5.34	5.21	5.81	6.25	8.70	-	-	-	-	*	*
R 5	4.44	3.83	4.63	5.46	6.25	7.19	7.94	8.70	9.80	11.11	11.90	13.16	14.29	16.94	17.24	18.18	.0809	.0825
R 6	4.82	6.90	7.75	8.20	8.40	9.01	9.25	10.00	10.75	11.76	12.35	12.66	13.16	14.29	14.93	15.62	.0468	.0454
R 7	4.76	3.25	3.68	3.80	3.98	(3.68)	4.35	(4.15)	4.81	5.13	5.49	5.85	5.95	6.62	7.14	7.58	.0240	.0268
R 8	4.55	4.13	4.50	4.52	4.58	4.65	4.72	4.78	4.88	4.93	5.02	5.05	5.10	5.21	5.32	5.24	.0048	.0042
R 9	4.93	3.51	3.94	4.11	4.44	4.76	4.98	5.24	5.59	5.95	6.37	6.71	7.04	7.35	7.69	8.13	.0244	.0237
R 10	4.96	3.50	4.48	6.45	8.93	10.42	14.08	16.67	20.0	23.8	27.8	31.2	34.8	38.5	40.0	43.5	.237	.226
R 11	4.87	3.51	4.72	5.65	9.26	11.90	14.29	16.67	20.4	23.8	27.0	28.7	33.3	37.0	40.0	43.5	.229	.221
R 12	4.85	3.28	5.38	7.58	9.90	12.34	14.71	17.24	20.4	23.8	27.0	30.3	(37.0)	37.0	40.0	41.7	.223	.215
R 13	4.82	3.20	3.79	4.10	4.55	5.15	5.43	5.88	6.21	7.30	8.06	8.56	9.52	10.20	10.99	11.63	.0473	.0496
R 14	4.86	3.37	6.71	9.17	13.16	17.24	20.8	25.0	30.3	37.0	40.0	50.0	55.6	62.5	66.7	73.5	.403	.411
R 15	4.83	3.40	5.23	6.99	8.85	10.31	-	13.16	15.62	17.86	20.0	22.2	24.4	26.3	28.6	31.3	.149	.147
R 16	4.82	3.38	3.75	4.08	4.39	4.67	4.98	5.35	5.85	6.33	6.85	7.30	5.75	8.26	8.77	9.26	.0325	.0324
R 17	4.85	3.52	4.48	5.41	6.45	7.58	8.70	9.71	11.36	12.82	14.29	15.87	17.24	18.87	20.0	21.3	.1002	.0969
R 18	4.83	3.41	3.95	4.26	4.63	5.00	5.35	5.71	6.21	6.71	7.04	7.69	8.70	8.77	9.17	9.62	.0341	.0337
R 19	5.11	3.13	3.55	3.65	4.76	5.52	6.45	7.30	8.70	10.20	11.76	13.16	14.75	16.39	17.86	19.23	.0978	.1006
R 20	5.10	3.21	4.27	5.23	6.54	7.75	8.93	10.10	11.76	13.33	14.71	16.40	17.86	19.23	20.6	22.2	.1046	.0998
R 21	4.76	1.01	3.47	6.41	9.80	12.50	16.13	19.23	24.4	28.6	33.3	38.5	42.6	47.6	52.6	56.8	.316	.314
R 22	5.07	2.28	5.23	8.93	12.66	16.39	20.0	23.8	-	-	-	-	-	-	-	-	.371	-
R 23	5.03	2.30	5.23	9.01	12.35	16.95	20.4	24.1	29.4	35.7	41.7	47.2	52.6	58.8	60.6	66.7	.367	.357
R 24	5.10	2.86	6.45	9.80	13.15	17.54	21.3	25.0	31.3	37.0	41.7	50.0	52.6	58.8	66.7	71.4	.385	.385
R 25	5.10	2.81	4.39	5.95	7.63	9.26	10.76	12.20	14.49	16.67	18.52	20.4	22.2	25.6	27.8	30.3	.148	.149
R 26	5.08	2.81	3.94	4.95	6.10	7.39	8.26	9.26	10.75	12.20	13.70	15.15	16.67	18.18	19.61	20.8	.0990	.0975
R 27	5.09	2.82	4.90	7.14	9.52	12.05	14.49	16.95	20.2	23.8	27.3	31.3	34.5	38.5	-	-	.239	.239
R 28	4.89	2.85	-	3.50	3.86	4.12	4.35	4.61	4.95	5.29	5.65	5.92	6.29	6.54	6.90	7.19	.0226	.0215
R 29	10.23	4.05	8.85	16.13	27.0	35.7	45.5	55.6	66.7	83.3	95.2	108.7	-	-	-	-	.920	.899
R 30	10.23	4.05	7.58	13.89	21.3	30.3	38.5	47.6	61.0	73.0	88.5	103.1	-	-	-	-	.891	.923
R 31	3.36	4.08	5.95	8.13	10.67	13.33	15.55	18.08	21.8	25.5	29.2	33.0	-	-	-	-	.248	.248
R 32	10.23	4.05	4.81	5.29	5.88	6.85	8.20	9.71	13.77	20.2	29.1	38.6	-	-	-	-	.324	.487
R 33	5.03	2.95	5.10	8.70	12.05	16.67	20.7	24.5	29.9	35.5	40.6	47.0	-	-	-	-	.380	.371
R 34	5.05	2.99	3.98	5.68	8.20	11.67	15.08	18.80	23.9	28.7	35.6	40.8	-	-	-	-	.356	.371
R 35	5.06	3.04	3.97	5.43	7.87	10.87	14.25	17.54	22.5	28.7	34.6	39.8	-	-	-	-	.351	.378
R 36	5.05	3.01	5.56	8.88	12.61	16.45	20.0	23.8	29.3	33.9	40.6	45.5	-	-	-	-	.366	.364
R 37	5.12	3.06	7.14	10.57	14.73	17.15	21.8	25.4	29.7	36.5	42.2	48.1	-	-	-	-	.373	.386
R 38	4.98	3.18	6.29	9.43	12.99	16.53	20.1	23.6	29.1	34.6		45.3	-	-	-	-	.361	.365
R 39	4.97	2.91	3.46	4.07	5.10	6.71	9.01	11.67	16.03	20.7	25.8	30.7	-	-	-	-	.274	.318

*Data distorted by iron dissolution from apparatus.

- Liquid flow rate - 1.6 to 7.6 liter/min
- Gas flow rate - 0.25, 0.75, 1.4 and 2.3 liter/min
- Total iron content - 3.3, 5 and 10 wt%
- Starting Fe^{+2}/Fe ratio - 0.15, 0.3, 0.45 and 1.0
- Final Fe^{+2}/Fe ratio - 0.23 to 0.009
- Gas/liquid mixing - residence time and velocity
- Reactor tank solution volumes - 0.5 and 1.5 liters

The experimental conditions under which the data of Table 23 were generated are shown in Table 24. Experiments in this table were arranged in groups of increasing reaction temperature within which reactant concentration and system geometry effects were investigated. Table entries are clear from the column titles, with the exception of entries in the last column. This column presents the computed rate constant for each experiment. The rate constant was derived from a regeneration rate expression which was determined to be of the form illustrated below. Derivation of the form of this rate equation will be discussed in a subsequent subsection of this report (§3.2.3.3.8).

$$r_R = K_R [Fe^{+2}]^2 [O_2]$$

where:

r_R = rate of disappearance of Fe^{+2}, mole/liter-min
$[Fe^{+2}]$ = concentartion of Fe^{+2}, mole/liter
$[O_2]$ = partial pressure of oxygen, atm
K_R = rate constant, liter/mole-atm-min

The tabulated K_R values were computed by least square fit of ferrous ion vs time data obtained during each regeneration experiment and measurement of solution density and system pressure; that is, the best linear fit of the data in a $1/Fe^{+2}$ vs t plot, where Fe^{+2} is expressed in moles per liter and t in minutes. The slope of such curve = K_R (partial pressure of oxygen constant). The rate constant can also be computed from the data in Table 23 if the "% Fe" values (second column) are converted to molar concentrations as follows:

wt% Fe	4.4	4.8	5.0	5.2	10.0	10.20	10.23
moles Fe/liter	0.93	1.02	1.06	1.10	2.54	2.60	2.61

Thus,

$$\text{Slope } \Delta(Fe/Fe^{+2})/\text{min} = K_R [O_2] Fe$$

TABLE 24. REAGENT REGENERATION EXPERIMENTAL CONDITIONS AND SUMMARY OF RATE CONSTANTS

Exp. No.	Gas	Pressure (psig)	Flow rate(1/min)		Apparatus(1)	Spent Reagent Feed(2)	$K_R \times 10^3$ (1/mol-atm-min)
			liquid	gas			
Nominal temperature = 70°C							
R 2	air	100	1.6	.25	Fig.9	nom.	2.5
R 8	air	100	4.6	.25	Fig.9	nom.	2.7
R 1	O_2	100	1.6	.25	Fig.9	nom.	1.8
R 9	O_2	100	4.6	.25	Fig.9	nom.	3.0
R 28	O_2	100	7.0	1.4	add FM	nom.	2.6
Nominal temperature = 100°C							
R 16	air	150	4.6	.75	Fig. 9	nom.	13.7
R 18	O_2	30	4.6	.75	Fig. 9	nom.	11.6
R 19	O_2	100	1.6	.25	add FM	nom.	11.9
R 20	O_2	100	1.6	.25	add FM	0.5 liter	12.0
R 17	O_2	100	4.6	.75	Fig.9	nom.	12.6
R 26	O_2	100	6.2	1.4	add FM	nom.	12.0
R 15	O_2	150	4.6	.75	Fig.9	nom.	13.0
R 25	O_2	150	7.0	1.4	add FM	nom.	12.4
Nominal temperature = 120°C							
R 7	air	100	1.6	.25	Fig.9	nom.	16.5
R 6	air	100	1.6	.25	Fig.9	15% Fe^{+2}	28.3
R13	air	100	4.6	.75	Fig.9	nom.	28.2
R 5	O_2	100	1.6	.25	Fig.9	nom.	11.3
R10	O_2	100	4.6	.25	Fig.9	nom.	28.2
R11	O_2	100	4.6	.75	Fig.9	nom.	28.5
R12	O_2	100	4.6	2.3	Fig.9	nom.	28.2
R27	O_2	100	7.0	1.4	add FM	nom.	28.6
R14	O_2	150	4.6	.75	Fig. 9	nom.	34.6
R24	O_2	150	7.0	1.4	add FM	nom.	32.0
R 22	O_2	150	4.6	.75	add FM	45% Fe^{+2}	30.9
R 23	O_2	150	4.6	.75	add FM	45% Fe^{+2}	30.9
R 21	O_2	150	4.6	.75	add FM	100% Fe^{+2}	28.5
R 32	O_2	150	1.6	.25	add FM	10% Fe	(3)
R 30	O_2	150	3.9	.75	add FM	10% Fe	30.5
R 29	O_2	150	7.3	1.4	add FM	10% Fe	30.8
R 31	O_2	150	7.6	1.4	add FM	3.3% Fe	33.0
R 34	O_2	150	1.6	.25	1/2"x33"	nom.	31.3
R 33	O_2	150	4.6	.75	1/2"x33"	nom.	31.3
R 35	O_2	150	1.6	.25	1/4"x33"	nom.	31.9
R 36	O_2	150	4.6	.75	1/4"x33"	nom.	30.7
R 37	O_2	150	3.6	.75	1/4"x160"	nom.	30.8
Nominal temperature = 160°C							
R 3	air	100	4.6	.25	Fig.9	nom.	14.9
R 4	O_2	100	1.6	.25	Fig.9	nom.	(4)

NOTES:

(1) The apparatus used in early runs is shown in Figure 9. After Exp.18, a flowmeter (FM) was added in the liquid loop as shown in the figure and the tubing was changed to 1/2 inch. In Exp.33 through 36 the packed bed was replaced by a piece of tubing. Exp.33 and 34 had a total of 33 inch of 1/2 inch tubing, while Exps.35 and 36 had the same length of 1/4 inch tubing. In Exp.37 the 1/4 inch tube was lengthened to 160 inches.

(2) Nominal conditions were: 1.5 liter of solution, 4.8 wt% iron, 30% of the iron as Fe^{+2}.

(3) Rate increased with time: 0-30 min, K=2; 30-60 min, K= 6; 60-90 min, K=12.

(4) Initital rate high, then almost level: 0-20 min, K=20; 20-120 min, K=3 to 5. Both runs at 160°C yielded large quantities of iron oxide and significant attack of the pump and equipment.

For example, K_R for Experiment R1 is computed as

$$K_R = \frac{0.0142}{(114.7/14.7)(1.035)} = 1.76 \times 10^{-3} \text{ liters/mole-atm-min}$$

or

$$K_R = \frac{0.0128}{(114.7/14.7)(1.035)} = 1.58 \times 10^{-3} \text{ liters/mole-atm-min}$$

The value given in Table 24 is 1.8 liters/mole-atm-min. In the majority of cases the first of the two listed slopes in Table 23 corresponds closer to the slope representing best all the data of each experiment, principally because it encompasses a larger portion of the data (larger time interval). Thus, in general, K_R's computed from this slope will be virtually identical to those listed in Table 24.

Table 24 clearly shows that the rate constant is independent of all parameters except temperature. (The few exceptions will be discussed below). The average rate constant measured at the three lowest temperatures are as follows:

Temperature, °C	K_R, liter/mole-atm-min
70	2.6×10^{-3}
100	12.4×10^{-3}
120	30.5×10^{-3}

The experiments were performed in the apparatus depicted in Figure 9. The apparatus consisted of a feed tank, which also served as a gas separator, a pump, a gas-liquid mixing tube (a length of stainless steel tube equipped with a tee for gas introduction), small packed bed, and a gas flowmeter. A liquid flowmeter was added during some experiments, while 1/2 inch and 1/4 inch diameter tubing (33 inches in length) was substituted for the packed bed during other experiments (see Table 24). A charge of 1.5 liters of ferrous/ferric sulfate solution was placed in the holding tank, circulated and brought to temperature, and the flow of oxygen or air was begun. Temperature was manually controlled and was generally held within ±2° of the nominal temperature for the duration of the experiment (±2° change in temperature at 70°C and 120°C corresponds to ±12% and ±9% changes in K_R, respectively). Pressure was controlled by a back pressure regulator which maintained the pressure to within ±2 to ±3 psi by continuously venting the excess gas.

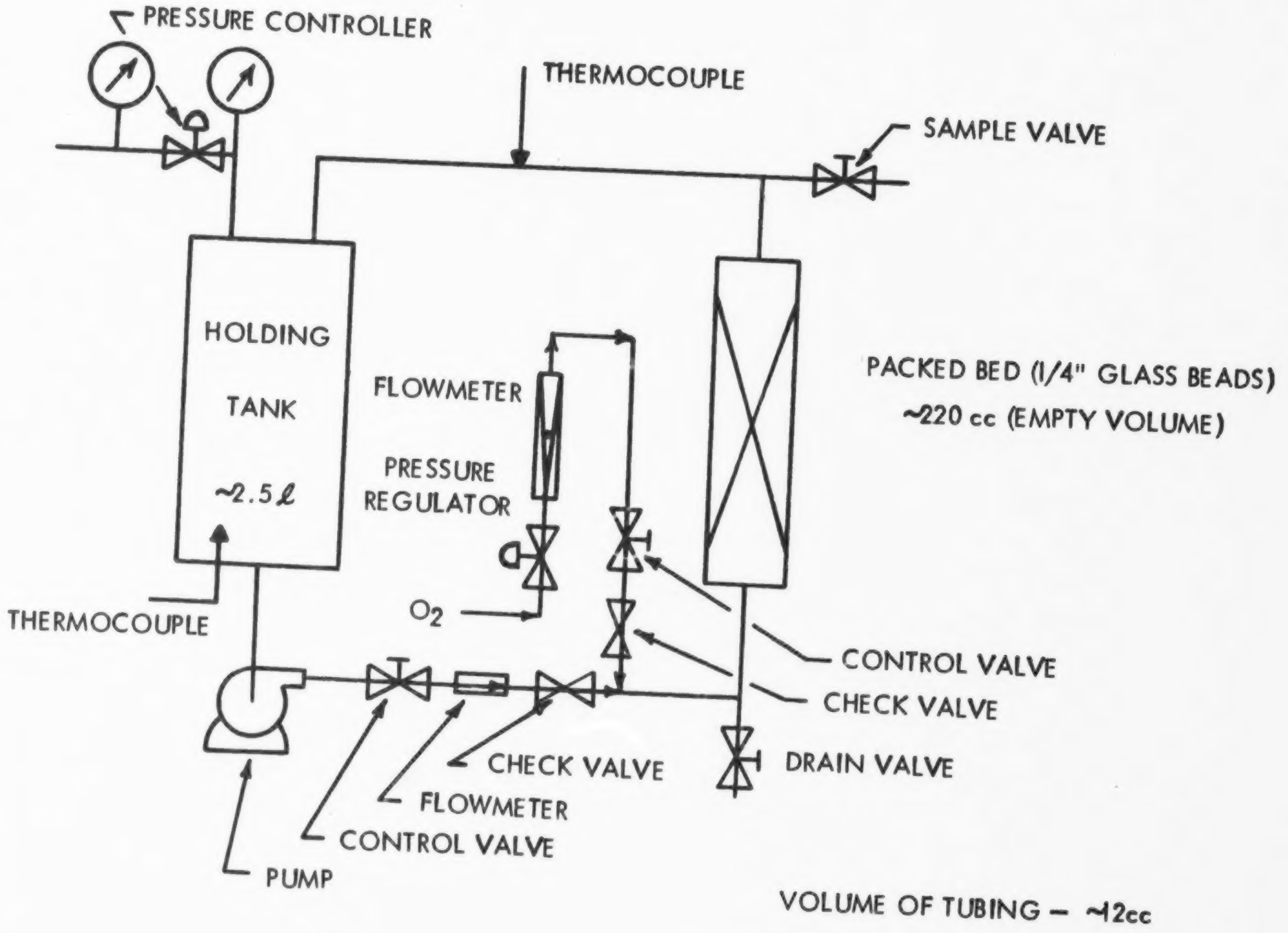

PRESSURE CONTROLLER
THERMOCOUPLE
SAMPLE VALVE
HOLDING
TANK
~2.5 ℓ
FLOWMETER
PRESSURE
REGULATOR
PACKED BED (1/4" GLASS BEADS)
~220 cc (EMPTY VOLUME)
THERMOCOUPLE
O_2
CONTROL VALVE
CHECK VALVE
CHECK VALVE
DRAIN VALVE
FLOWMETER
CONTROL VALVE
PUMP
VOLUME OF TUBING – ~12cc

FIGURE 9. FERRIC ION REGENERATION APPARATUS

It is believed that the system operated as follows: the oxygen or air was dispersed in the circulating liquid in the form of very tiny bubbles. The aerated liquid was reintroduced into the holding tank where it mixed with the liquid already present. The complete volume of liquid in the holding tank was therefore undergoing reaction as long as the solution was circulated and aerated sufficiently often to maintain fine bubbles throughout the liquid. When the frequency of circulation was too low, particularly under conditions where the oxygen consumption rate was high, the rate of regeneration began to decrease (insufficient oxygen feed rate and loss of oxygen due to increased residence time in tank, thus liquid-gas separation). For example, Experiment R13 (Table 24) which circulated 4.6 liters/min of 30% ferrous ion (5% total iron) at 120°C gave a rate constant of 28.2×10^{-3}. When the circulation rate was decreased to 1.6 liter/min in Experiment R7 the rate constant decreased to 16.5×10^{-3}; however, the rate constant returned to 28.3×10^{-3} when the starting solution was 15% ferrous ion (5% total iron) probably owing to the lowered oxygen requirement for the reaction.

At the lower temperatures (70°C and 100°C) the rate constant was not significantly influenced by dropping the liquid circulation rate as low as 1.6 liter/minutes. The lower oxygen consumption rate at lower temperature allowed the reaction to proceed at normal rate.

Gas flow rates in the range of 0.25 to 2.3 standard liter/minute (see Exps.R10, R11, and R12) did not influence the rate constant. All runs had adequate gas-liquid mixing and the performed changes in circulation loop velocity and geometry had no influence on the rate constant.

Changes in the starting ferrous ion content (15% to 100%) and the total iron content (3.3% to 10%) had little observable influence on the reaction rate.

One experiment was performed in which regeneration of ferric ion took place concurrently with pyritic sulfur leaching from a Lower Kittanning coal sample. The generated data was presented earlier (Exp.64, Table 22) in conjunction with the data from the coal leaching experiments. The experiment was performed in the apparatus depicted in Figure 10 which is a slightly modified version of the regenerator previously shown in

Figure 9. The Figure 10 apparatus did not include a packed bed and the loop tubing was changed to 1/2 inch diameter to allow for continuous circulation of -100 mesh coal. This same apparatus was used for pressurized coal leaching under nitrogen. The concurrent coal leaching/reagent regeneration experiment was part of the small matrix of probing tests aimed at defining potential process improvements. The obtained results discussed in the next section appear very promising.

3.2.3.3 Discussion of Results

The parametric investigations performed on the Meyers' process for the pyritic sulfur removal from coal, described in detail in the previous section, revealed the following:

- Important parameters affecting the leaching efficiency are: coal particle size, leaching temperature and time, the ferrous ion to total iron ratio in the reactor (leacher), and the total iron concentration of the system.
- The mode of leacher operation (batch, multi-batch, continuous, or continuous followed by batch) affects process efficiency only to the extent that it influences the value of the ferrous ion to total iron ratio, and this effect is especially pronounced early in the reaction.
- Hot slurry filtration is not influenced by coal particle size under the conditions investigated (vacuum filtration of four liter systems). It is believed, however, that the system volume was too small for adequate evaluation of the filtration operation; thus, extensive parametric investigation of this unit was not performed. For process design purposes available commercial data on liquid-solid separations was utilized.
- Three-stage hot water washing (80°-90°C) was found adequate for reagent removal from processed coals under atmospheric pressure. Coal particle size did not have a measurable effect on washing efficiency. Washing efficiency appeared to improve with increasing quantity of water and number of washing stages. As in the case of filtration, more precise parametric information on this unit operation should await pilot plant experimentation. The bench-scale system volume is too small for determining the best mode of operation of this unit. Process experiments with pressurized coal leaching above 120°C indicated that washing water pH may also be an important parameter of this unit operation due to iron oxide formation during leaching and during combined leaching/regeneration.

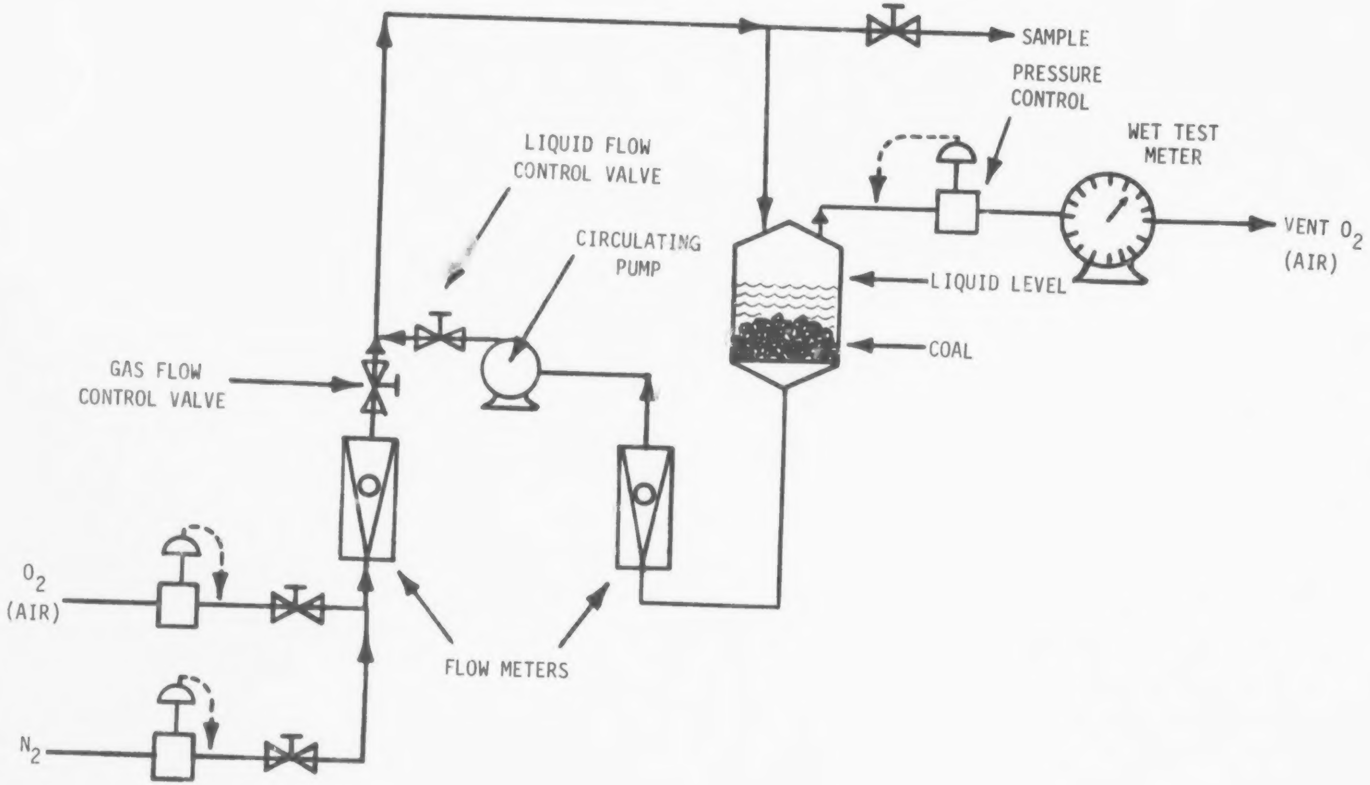

SAMPLE
PRESSURE CONTROL
WET TEST METER
LIQUID FLOW CONTROL VALVE
CIRCULATING PUMP
VENT O_2 (AIR)
LIQUID LEVEL
COAL
GAS FLOW CONTROL VALVE
O_2 (AIR)
N_2
FLOW METERS

FIGURE 10. PRESSURIZED LEACHER - REGENERATOR SYSTEM

- One hour reflux extraction with toluene proved sufficient for complete elemental sulfur recovery from processed coal. Process improvement tests indicated that the same quantity of toluene removes (with identical efficiency) the elemental sulfur from leached coal before or after washing. Indications are that the limited experimental range utilized in this unit operation with respect to solvent volume, solvent nature and extraction temperature leaves substantial room for unit operation optimization.

- Coal drying under vacuum at 100°C for five hours proved sufficient to completely remove the toluene and/or water retained by the coal during processing (regardless of the mesh size in the investigated range). This unit operation may be redundant to the pyritic sulfur removal process if elemental sulfur recovery is performed prior to coal washing and if the ultimate user of the coal could tolerate approximately 20% moisture content.

- Important parameters affecting the ferric ion (reagent) regeneration proved to be: ferrous ion concentration, oxygen partial pressure, regeneration temperature, and liquid-gas mixing efficiency.

The ensuing paragraphs discuss in detail each of the important parametric effects, their qualitative trends and the quantitative dependence of the process rate on them. Process rate expressions are developed for the pyritic sulfur leaching and reagent regeneration operations. Process design curves are generated and discussed. The results of the process improvement test matrix are analyzed and their expected impact on the process is presented.

The data used in this section were abstracted from the data tables presented in the last section and included in Appendix B of Volume 2 of this report. Each entry is appropriately labeled for easy reference to the source. It should be noted that process and element mass balances throughout the investigation were excellent and furnished confidence in the generated data. In addition, balances on key elements (such as sulfur) were checked by at least two independent means of determination. As indicated earlier, pyritic sulfur removals were computed from at least three independent data sources (total coal sulfur, sulfur forms, iron forms), with "recovered sulfur" data being used occasionally. Early in the investigation duplicate experiments were performed for added confidence. Questionable analyses were rerun when possible.

3.2.3.3.1 Coal Particle Size Effect on Pyritic Sulfur Removal from Coal

Table 25 indicates the effect of coal particle size on extent of pyritic sulfur removal from Lower Kittanning and Illinois No. 5 coals extracted for four hours at 102°C with 1M ferric chloride solution (approximately 5 wt. % in ferric ion) in a batch mode.

Table 25. Coal Particle Size Effect on Pyritic Sulfur Removal

Coal Top Size	Lower Kittanning			Illinois No. 5		
	% Sulfur Removal*	Reference		% Sulfur Removal*	Reference	
		Exp. No.	Table		Exp. No.	Table
1/4 inch	37	12 & 13	20 (Pt. IV)	48	5 & 6	20 (Pt. IV)
14 mesh	62	10 & 11	20 (Pt. IV)	39	3 & 4	20 (Pt. IV)
100 mesh	68	7 & 8	20 (Pt. IV)	46	1 & 2	20 (Pt. IV)

*Based on before and after processing total sulfur analyses. Average values of two runs.

The entries of this table indicate that there is a substantial particle size effect between -100 mesh and -1/4 inch Lower Kittanning coal, but a much smaller effect between -100 and -14 mesh coal. On the other hand, no particle size effect is observed with the Illinois No.5 coal. A firm conclusion regarding particle size effects of Illinois No.5 coal would be inappropriate at this time since analysis of the spent reagent revealed that the -1/4 inch samples of Illinois No.5 coal had consumed 80% of the available ferric ion while the -14 and -100 mesh coal samples had consumed virtually all available ferric ion (Lower Kittanning coal samples consumed between 20% and 60% of the charged ferric ion). The depletion of ferric ion during the Illinois No.5 experiments casts doubt on any conclusion concerning particle size effects on pyritic sulfur removal from this coal by extraction with ferric chloride. Indirectly, one may infer that there is a particle size effect with this coal since -1/4 inch samples did not consume all the available ferric ion while -14 and -100 mesh samples did. Further coal particle size effect investigations with Illinois No.5 coal were not performed.

Additional coal particle size effect experiments were performed with the Lower Kittanning coal during ferric sulfate extractions. The results were strikingly similar to those shown in Table 25. Practically identical values were obtained after four hours of extraction under the same operating conditions. Figure 11 shows the effect of coal top size on both the rate and extent of pyritic sulfur removal from Lower Kittanning coal. The data indicates that this effect is substantial between 1/4 inch and 14 mesh top size coal samples extracted under identical experimental conditions but diminishes with further decrease in coal top size. Effects on -100 and -200 mesh coal must be considered zero within experimental repeatability. Since both pyrite leaching rate and reaction extent increase with decreasing coal top size to -100 mesh, this coal size is indicated as the optimum size for removal of pyrite from Lower Kittanning coal under processing conditions of atmospheric pressure, 102°C, and pure ferric sulfate leach solution.

It is important to point out that the effect of particle size on pyrite removal rate may be much smaller for coals with finely disseminated pyrite particles rather than the relatively large, low surface area/weight ratio aggregates visible to the naked eye in the Lower Kittanning and Illinois No.5 coals used in this study.

3.2.3.3.2 Extraction Temperature Effect on Extent and Rate of Pyritic Sulfur Removal from Coal

Table 26 indicates the temperature effect on the extent of pyritic sulfur removal from -100 mesh Lower Kittanning coal extracted with a 5 wt% iron solution of pure ferric sulfate.

Table 26. Pyritic Sulfur Removal as a Function of Temperature

Extractions		Pyrite Removed (Wt%)	Extraction Time (Hours)	Pyrite Removed (wt%)	Reference
Temp. (°C)	Time (hours)				
70	6	48*	12	69* 70**	Exp.52
85	6	69*	12	85* 89**	Exp.51
102	6	72*	12.7	90* 92**	Exp.50
130	4	81**			Exp.63

*Based on iron analysis

**Based on before-and-after processing sulfur form analysis

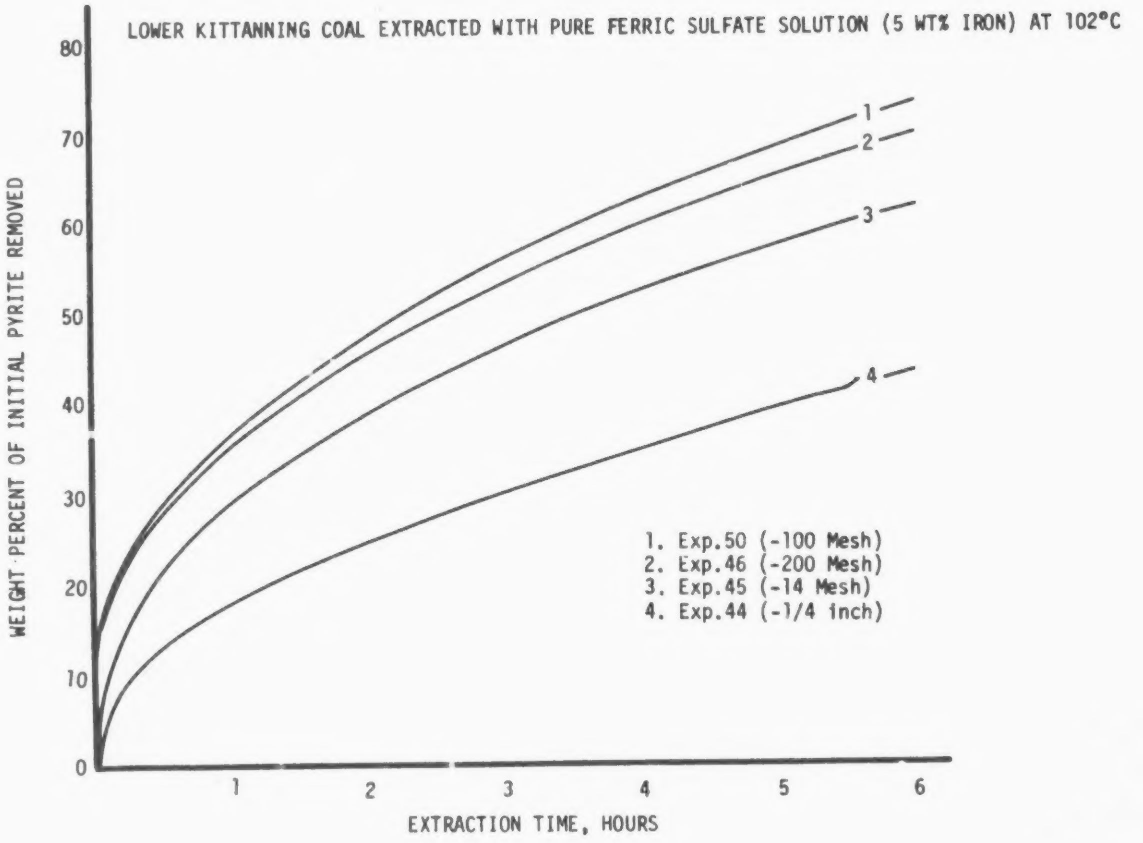


FIGURE 11. EFFECT OF COAL PARTICLE TOP SIZE ON PYRITIC SULFUR REMOVAL

The effect is indicated at two reaction times. In both cases the extent of pyritic sulfur removal increases dramatically with temperature. Between 70°C and 130°C sulfur removal almost doubles; however, the disproportionately small difference between removals obtained at 85° and 102°C can not be firmly explained. Figure 12 indicates the temperature effect on pyrite leaching rates. Rate data on Experiment 63 is not available due to formation of solid iron compounds during extraction; however, the four hour data point obtained from sulfur form analysis of the processed coal indicates that the 102°C curve lies about equidistant between the 130°C and 70°C curve. This would be expected if the rate constant obeyed the Arrhenius equation for temperature dependence. Such a dependence of rate constant on temperature would suggest that pyritic sulfur extraction from 100 mesh top size Lower Kittanning coal may not be a diffusion controlled process.

3.2.3.3.3 Effect of Residence Time on Pyritic Sulfur Removal from Coal

The effect of leacher residence time on the extent of pyritic sulfur removal from coal under all experimental conditions utilized in this program is positive. That is, sulfur removal increases with increasing residence time. Figures 11 and 12 illustrate this parametric effect. However, these plots indicate that the rate of sulfur removal (the slope of the curves in Figures 11 and 12) continuously decreases with time. The rate decreases sharply after the first few minutes of reaction and tapers off to a small percentage of the initial rate at residence times in excess of 4 to 6 hours (depending on experimental conditions).

This type of rate behavior implies strong dependence of rate on the concentration of depleting reactants. Since all bench-scale data exhibited similar type of behavior and the only depleting reactant common to all tests was pyrite, a conclusion may be drawn that the rate is a strong function of the pyrite available for reaction. Computer analysis of all the data obtained from the extraction of -100 mesh Lower Kittanning coal (Experiments 47 through 50 and 54 through 59) at 102°C revealed that the pyritic sulfur leaching rate is proportional to the square of the pyrite concentration in coal.

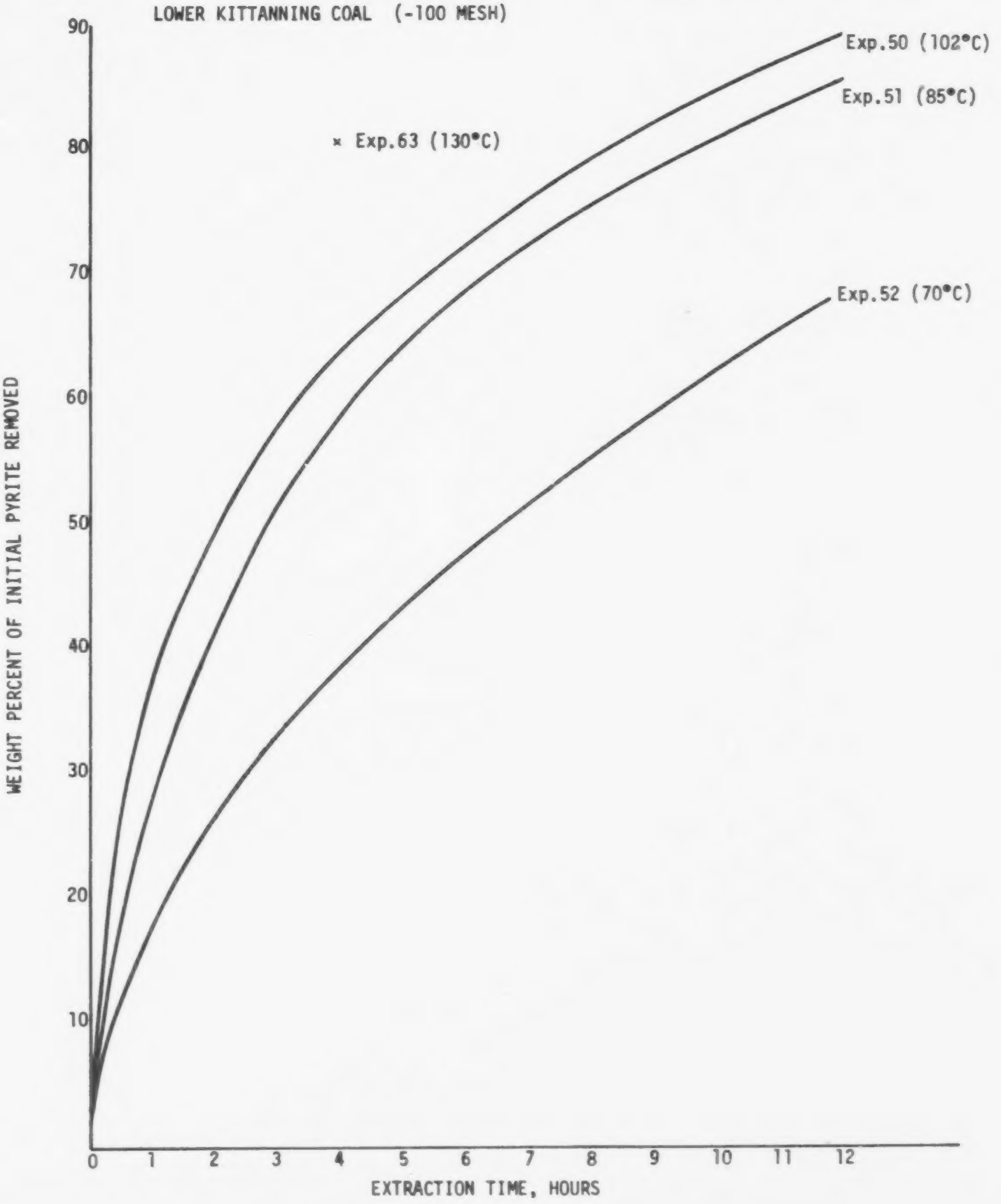


FIGURE 12. TEMPERATURE EFFECT ON PYRITIC SULFUR REMOVAL

3.2.3.3.4 Ferrous Ion to Total Iron Ratio Effect on Extent and Rate of Pyritic Sulfur Removal from Coal

The ferrous ion to total iron ratio has a pronounced effect on both the rate and extent of pyritic sulfur removal. Both quantities decrease with an increase in this ratio. The effect is illustrated in Figure 13.

Curve A represents the average of the rate data from Experiments 50, 55, 56 and 57. These experiments were performed under the continuous reagent exchange mode. That is, pure ferric sulfate solution (solution that did not contain ferrous ions) was continuously added to the reactor and an equal amount of spent reagent was withdrawn from it at a predetermined rate schedule. The only differences among the experiments of Curve A was the total iron content of the reagent charge and the rate and duration of exchange. They are represented by a single curve because the ferrous ion to total iron ratio in the reactor during the entire leaching period of these four experiments remained between 0.0 and 0.35. These experiments simulated continuous exchange leaching followed by batch leaching operations (see Table B-3 for actual schedules).

The data from Experiment 49 was obtained in the same fashion as that of Curve A, except that the charged reagent was a mixture of ferric and ferrous salt solutions ranging in composition from 48% to 89% ferric ion. That is, the reactor was initially charged with an iron sulfate solution of Fe^{+3}/Fe ratio (defined from hereon as Y) equal to 0.48. Solutions continuously increasing in Y were then added until the initial 3 hours of reaction time had been completed. Iron sulfate containing 89% of the iron in the ferric ion form was added thereafter. The ferrous ion to total iron ratio (1.0-Y) in the leacher varied from 0.52 at t=0 to 0.20 at t=12 hours. This mode of operation simulated countercurrent leaching.

The data from Experiments 47 and 48 was obtained under the batch mode of operation. That is, the initial reagent charge was not replaced during the experiment. Thus, Y continuously dropped because of ferric ion consumption and ferrous ion production. The difference between the two experiments lies in the composition of the reagent charge. Experiment 48 was charged with reagent of Y=0.86; the 1-Y ratio during the 4-hour extraction varied from 0.14 at t=0 to 0.62 at t=4 hours.

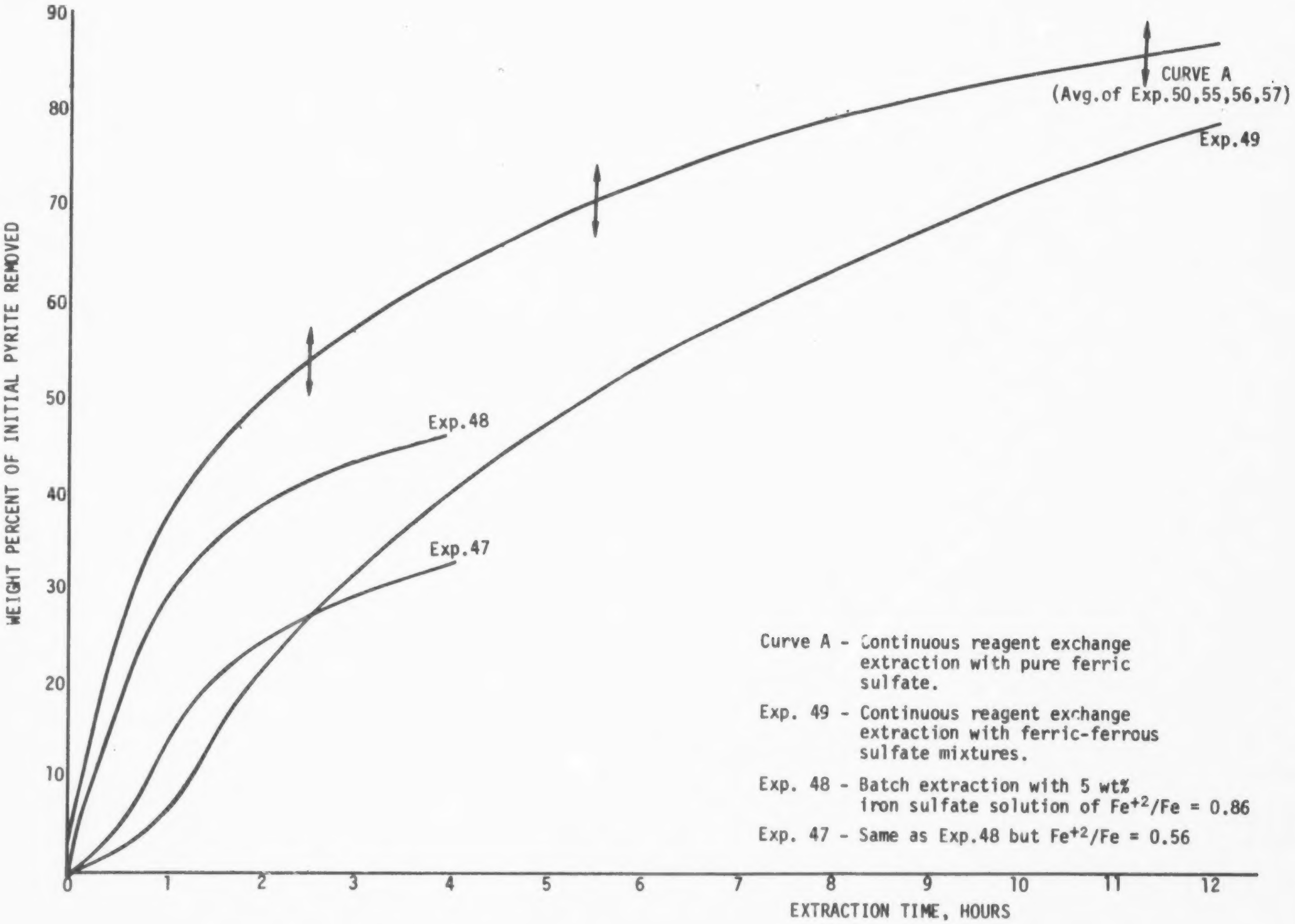


FIGURE 13. EFFECT OF Fe^{+2}/Fe ON PYRITIC SULFUR REMOVAL FROM -100 MESH LOWER KITTANNING COAL

Experiment 47 was charged with reagent of Y=0.56 and during the reaction the ratio 1-Y varied from 0.44 to 0.68 at t=4 hours.

Figure 13 clearly indicates that batch operation of the leacher is not desirable and counter-current operation of the leacher may not be the best because of the adverse effect that ferrous ion to total iron ratios greater than 0.35 have on the rate of pyritic sulfur extraction. Ideally, this ratio should be kept near zero. The effect of this quantity is most severe during the early stages of reaction when the rates of ferrous ion production and ferric ion consumption are high. The process may conceivably be operated, therefore, in a continuous exchange mode until 60 to 70 percent of the pyrite is removed and then switched to batch mode. Experiments 55 through 57 were operated in this combined mode and, as Figure 13 indicates, the removal rates differed only slightly from those obtained when exclusively employing a continuous exchange operation (Experiment 50). In fact, sulfur form analyses of the processed coal indicated identical pyrite removals of 91% to 92% for Experiments 50, 55 and 56, while Experiment 57 showed 87% removal.

The concentration of ferrous ion in the reactor is, in itself, not important with respect to pyritic sulfur removal rates; rather, the ferrous ion to total iron ratio (the ratio of the iron forms) is the important factor affecting reaction rate. Computer analysis of all the data indicated that the pyritic sulfur leaching rate from Lower Kittanning coal is proportional to the square of the Fe^{+3}/Fe ratio.

3.2.3.3.5 Total Iron Concentration Effect on Pyritic Sulfur Removal from Coal

The effect of total iron was repeatedly investigated throughout the program because of conflicting results. The effect, if any, appears to be minor; however, if present, the effect is believed to be due to differences in reagent solution viscosity. Table 27 summarizes representative data generated during the investigation of this effect.

With the exception of two entries that were derived from ferric chloride extractions, the data in Table 27 were obtained from ferric sulfate extraction of coal samples at 102°C. Five pyritic sulfur removal values were computed from iron analyses (coal analysis values not available) while all others were computed from coal analyses. The three values labelled "adjusted" were corrected for the percent difference between pyritic sulfur removal values derived from iron and coal analyses at the end of extraction (12.5 hours).

Table 27. Total Iron Effect on Pyritic Sulfur Removal

Total Iron (wt%)	Coal Top Size	Extraction Time (Hours)	Pyritic Sulfur Removal (wt%)	Extraction Time (Hours)	Pyritic Sulfur Removal (wt%)	Reference (Exp.Nos.)
A. LOWER KITTANNING COAL						
3.8	100 mesh	4	62**+	12.5	90	54
5.0	100 mesh	4	70**+	12.5	92	55
~5*	100 mesh	4	67			7 & 8
6.7	100 mesh	4	65+	12.4	92	56
7.9	100 mesh	4	61+	12.4	87	57
10.8	100 mesh	4	60**+	12.5	87	58
~12*	100 mesh	4	67			20 & 21
B. ILLINOIS NO.5 COAL						
5.0	1/4 inch	8	46			33,34,36
2.5	1/4 inch	8	26			38

*Ferric chloride system.
**Adjusted values.
+Computed from iron analysis.

Examination of Lower Kittanning data in Table 27 could lead to three different conclusions: (a) there is no total iron effect - the observed differences in sulfur removal values are normal experiment repeatability variances; (b) there is a small "dome" effect - sulfur removal increases with total iron for reagent iron concentrations of 3.8 to 5.0 wt% and decreases when the reagent iron concentration exceeds 5.0 wt%; (c) pyritic sulfur removal decreases as reagent total iron concentration increases with the first and last four-hour entries being outliers. If the last conclusion is correct, the rate becomes inversely proportional to total iron concentration expressed in weight percent. This represents the maximum effect derived from the above data.

The data from Illinois No.5 coal indicate significant total iron effect, with pyritic sulfur removal approximately doubling with two-fold increase in reagent total iron concentration. However, the data is insufficient for definite conclusions. Furthermore, the discrepancies in analysis observed with this coal and the excess consumption of ferric ion increase the uncertainty of any conclusion.

The only safe conclusion that can be drawn at this time concerning the total iron effect is that additional experimentation is needed with duplicate or triplicate experiments for each iron concentration. It should be noted that this effect, if present, is independent of the ferrous ion to total iron ratio.

3.2.3.3.6 Other Effects on Pyritic Sulfur Removal from Coal

As indicated earlier, the leacher was operated under several processing modes in order to investigate the effect of processing parameters on pyritic sulfur removal. The generated data indicated that the mode of leacher operation influences pyritic sulfur leaching only because each mode produces a different level of ferric ion to total iron ratio (Y) in the reactor at a given reaction time and with all other parameters being equal. Thus, the mode of leacher operation has an indirect effect on pyritic sulfur removal rates.

In addition to the continuous exchange, continuous exchange followed by batch, continuous counter-current, and batch modes, a counter-current multi-batch mode of operation was investigated. During this type of operation the spent reagent solution was drained from the leacher every two hours and replaced with preheated fresh solution. Initially, the reactor was charged with a leach solution of approximately Y=0.50; every subsequent charge was made with an increasingly higher Y. This mode of operation (Experiment 53) differed from the continuous counter-current mode (Experiment 49) in that additions and withdrawals of reagent were periodic and not continuous. However, because of the fact that the spent solution was completely withdrawn every two hours, the increase of Y in the reactor was faster than that observed in Experiment 49 and the obtained pyritic sulfur removal was higher. The large number of filtrations which would be required for multi-batch operation renders this mode impractical for small sized coal processing.

The majority of coal sample extractions were performed with reagent solutions prepared from "reagent Grade" iron chloride and iron sulfate salts. However, the effect of using "Commercial Grade" ferric sulfate was investigated. A sample of 1/4 inch top size material from each coal (Lower Kittanning and Illinois No.5) was extracted at 102°C for 4 hours with Ferri-Floc solutions containing approximately 5 wt% iron. Ferri-Floc is a commercial grade ferric sulfate salt used for waste water treatment. In its dry form the salt is basically composed of 90% ferric sulfate, 5% ferrous sulfate and chloride, and 5% insolubles (principally silicates). The attained sulfur removals with Ferri-Floc were virtually identical to those obtained from equivalent extractions with pure ferric sulfate or chloride as shown below:

	PYRITIC SULFUR REMOVAL WT%	
	Lower Kittanning	Illinois No.5
Ferri-Floc Solution	37	42.4
Reagent Grade Solution	35	47 (ferric chloride)

The conclusion drawn was that commercial ferric sulfate is just as efficient a pyritic sulfur removal reagent as pure ferric sulfate. The full impact of this conclusion is realized when considering that the mineral derived leach solution (Ferri-Floc) is expected to contain many of the minor constituents which may be present when the coal leach solution is repeatedly circulated and regenerated.

Another effect investigated was coal weathering. Samples of 100 mesh top size Illinois No.5 and Lower Kittanning coals were artificially weathered by refluxing coal/water slurries for 4 hours with oxygen continuously flowing through the slurry. An assumption was made that the artificial weathering simulated natural coal weathering. The wet coals were subsequently extracted with ferric chloride solution in the usual manner. The sulfur removal values obtained were compared to removal results from identical extractions of unweathered coal. Resultant data in Table B-1 of Appendix B, Volume 2 (Experiments 20 through 27), indicate that the Meyers' Process for pyritic sulfur removal is equally efficient with weathered coal as it is with freshly mined coal. In addition, these experiments revealed that artificial weathering does not reduce the excess ferric ion consumption during ferric chloride extraction of freshly mined Illinois No.5 coal.

3.2.3.3.7 Leaching Rate Expressions and Leacher Design Curves

The parametric investigations discussed above revealed that the pyritic sulfur extraction rate from Lower Kittanning and, with less certainty, Illinois No.5 coals, is a function of

- Coal particle top size
- Temperature, T
- Concentration of pyrite in the coal at time t, W_p
- The ferric ion to total iron ratio in the reactor at time t, Y.

Thus, it was assumed that the pyritic sulfur leaching rate could be represented by the expression

$$r_L = -\frac{dW_p}{dt} = K_L W_p^{A} Y^{B} \qquad (9)$$

where

r_L	is the pyritic sulfur leaching rate, expressed in weight of pyrite removed per 100 weights of coal per hour
W_p	is the pyrite concentration in coal at time t in weight percent
t	is reaction (leaching) time in hours
K_L	is the reaction rate constant, in $(\text{hours})^{-1}$ $(\text{wt\% pyrite in coal})^{1-A}$
Y	is the ferric ion to total iron ratio in the reactor (leacher) at time t, dimensionless

A & B are reaction orders with respect to W_p and Y, respectively.

A computer program was written which utilized available data on W_p and Y as a function of reaction time and which assumed values of A and B between 0.5 and 3 to compute K_L. The constancy of K_L for a given reaction temperature and coal top size was the criterion for the selection of the A and B values to be utilized in eq 9.

The entire set of data generated from -100 mesh Lower Kittanning coal sample extractions with iron sulfate at 102°C was computer-fitted to Expression 9 (Experiments 47 through 50 and 54 through 59). These data were generated under various modes of leacher operation at widely varying values of Y. Reaction constants were computed for every data point of each experiment (usually every fifteen minutes of reaction time). The constancy of K_L within each experiment and between experiments was evaluated.

The best fix of data (K_L value closest to "universal" constancy) was obtained with values of A=2 and B=2. For these reaction orders the K_L values within each experiment varied by less than ±25% in a random manner; considering normal data scatter such constancy is at least adequate. The difference in K_L values between experiments was even smaller. In fact, K_L values from experiments performed with reagent solutions of total iron concentrations near 5 wt% differed by less than 10 percent.

Thus, the derived empirical rate expression for the removal of pyritic sulfur from Lower Kittanning coal by leaching with ferric salts is

$$r_L = -\frac{dWp}{dt} = K_L Wp^2 Y^2 \qquad (10)$$

where K_L is a function of temperature and coal particle size. Strictly speaking, Equation (10) is valid only for extractions involving

- Lower Kittanning coal
- Y values between 1 and 0.30
- Reagent total iron concentration between 4 and 10 wt%
- Iron sulfate reagent

It can be safely assumed, however, that Expression (10) applies to coal extractions with ferric chloride and possibly Illinois No.5 coal which is processed under similar conditions, provided the excess consumption rate of ferric ion is considered in determining the value of Y. This speculative extension of rate expression applicability is based on similarity of reaction rate curves or pyritic sulfur removal values.

The rate constant value for 100 mesh top size Lower Kittanning coal extracted with ferric sulfate solution containing 5 ±2 wt% total iron, at 102°C, is

$$0.12 \leq K_L \leq 0.15 (\text{hours})^{-1} (\text{wt\% pyrite in coal})^{-1}$$

The K_L value is closer to 0.12 if pyritic sulfur removals are computed from iron analysis and approximately 0.15 when the sulfur removal values are based on total sulfur and sulfur form analysis of before-and-after processing coal. Actually, there is at least a 25% uncertainty with either of the above K_L values so that the reported range is insignificant.

Temperature effect data indicated that the rate constant is of the form

$$K_L = A_L \exp(-E_L/RT) \tag{11}$$

where

$$A_L = 2 \times 10^3 (\text{hr})^{-1} (\text{wt\% pyrite in coal})^{-1}$$

and

$$E_L = 7 \text{ Kcal/mole}$$

The values of A_L and E_L are based on two temperature points and thus, they are approximate. However, the present rate data indicates that the rate doubles between 70°C and 102°C and that it may double between 102°C and 130°C; that is, for the same percent of pyrite removal the 70°C extraction time is twice that of the 102°C extraction time, and so on (see Figure 12).

It was estimated that the K_L value for the leaching of pyritic sulfur from 14 mesh top size Lower Kittanning coals is approximately 25% lower than that computed for the extraction of -100 mesh coal at the same reaction temperature.

The developed empirical rate equation, Expression (10) and the computed value of the reaction constant served as the basis for the generation of the process design curves shown in Figure 14. These curves comprise the fundamental information for the pyritic sulfur removal process commercial size plant design discussed in a later section. They also represent some of the basic pieces of information required for any scaled-up design of the process.

Simultaneously with the development of the empirical formulation for process leaching rate an effort was undertaken to determine an expression for the rate of pyritic sulfur leaching from coal based upon theoretical reaction modeling. The constructed simple rate model was based on the following mechanistic assumptions:

- The rate of reaction depends entirely on the pyrite surface area available for reaction provided larger than stoichiometric quantity of ferric ion is present in the reactor at all times (Fe^{+3} moles >9.2 times moles of the pyrite present in the reactor, as determined from process chemistry).
- The coal matrix does not influence the rate of reaction.

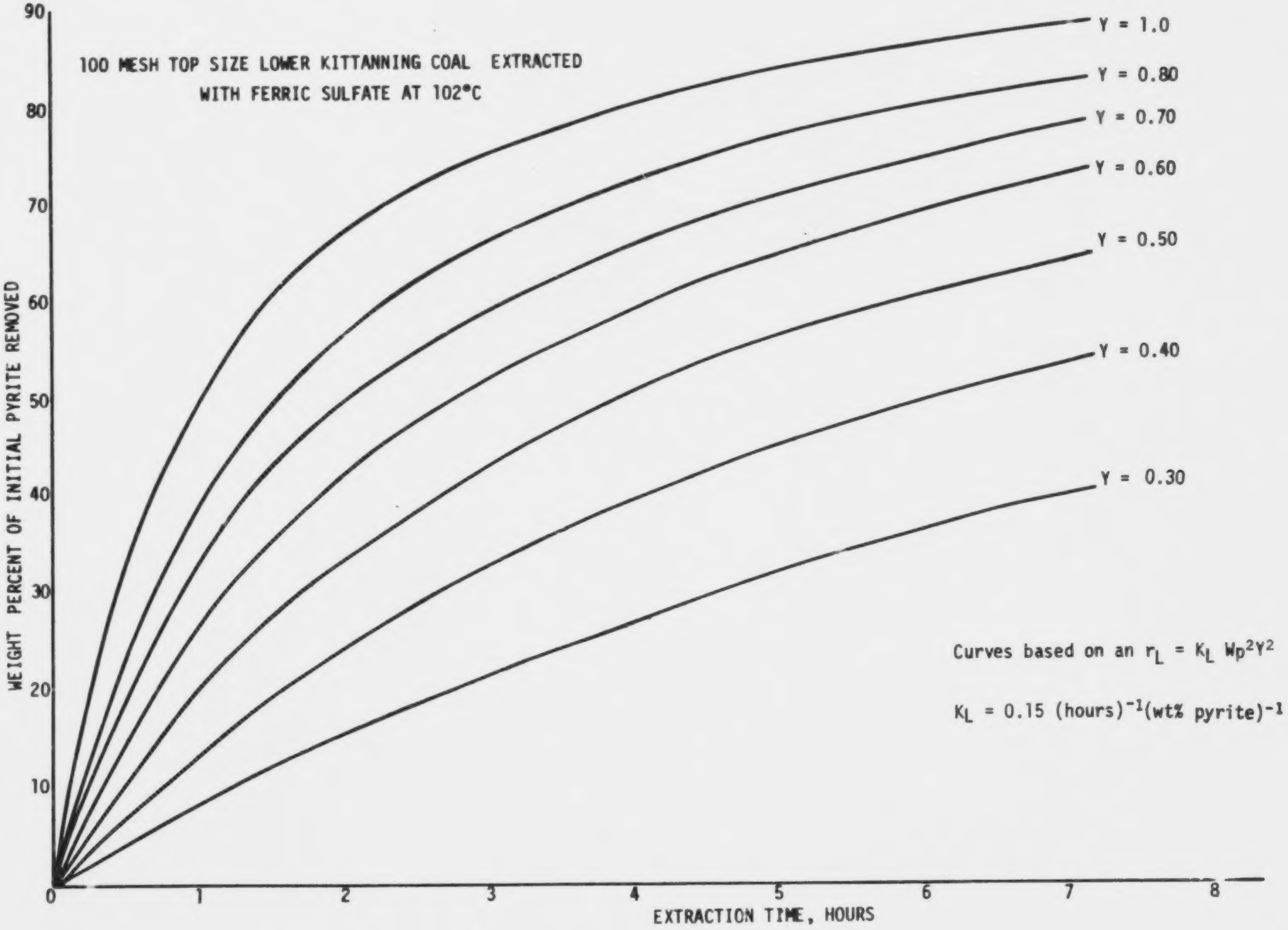


FIGURE 14. PYRITIC SULFUR LEACHER DESIGN CURVES

- The pyrite surface available for reaction is only a function of the average pyrite particle size, or its size distribution, and Y. Thus,

  $$(Sp)_{avail.} = (Sp)_{total}\,(Y)$$

  for a given average pyrite particle size.
- The pyrite particle size distribution is proportional to that of the coal. The rate depends on this distribution only for coals of top size >14 mesh. That is, top size coals of 100 mesh and 200 mesh react with approximately the same rates if all other reaction parameters are identical.
- Pyrite particles in the coal can be approximately by spheres and for a given top size coal an average radius, $\overline{R}_p$, can be assigned to them.

Under the above assumptions, the pyritic sulfur leaching rate per unit available pyrite surface, J_L, is constant at constant temperature and coal top size; that is,

$$J_L = \left(\frac{1}{4\pi\overline{r}_p^2}\right)_{avail.}\left(-\frac{dWp}{dt}\right) = \left(\frac{1}{4\pi\overline{r}_p^2}\right)_{avail.}(r_L) = \text{constant} = k_1$$

where

$\overline{r}_p$ is the value of $\overline{R}_p$ at reaction time t.

But

$$\left(4\pi\overline{r}_p^2\right)_{avail.} = \left(4\pi\overline{r}_p^2\right)_{total}(Y) \quad \text{and}$$

$$4\pi\overline{r}_p^2 = 4\pi\overline{R}_p^2\left(\frac{\overline{r}_p}{\overline{R}_p}\right)^2 = \left(4\pi\overline{R}_p^2\right)k_2\,Wp^{2/3};$$

that is, the average radius of the pyrite particles in coal is proportional to the cube root of pyrite weight at time t, or $\overline{r}_p/\overline{R}_p = (\text{constant})(Wp/W_p^0)^{1/3}$ where W_p^0 is the percent pyrite in the feed coal. Thus,

$$J_L = \left[1/(4\pi\overline{R}_p^2 k_2 Wp^{2/3})\right](1/Y)\left(-\frac{dWp}{dt}\right) = k_1, \text{ or}$$

$$-\frac{dWp}{dt} = 4\pi\overline{R}_p^2 k_1 k_2 W_p^{2/3}\,Y = k_L\,W_p^{2/3}\,Y \qquad (12)$$

It is interesting to note that the empirical and theoretical rate expressions are identical in form and reactant dependency; the magnitude of the latter (reaction with respect to Wp and Y), however, is different. Model refinement is required, especially with respect to the use of a single average pyrite radius for a given coal top size.

3.2.3.3.8 Reagent Regeneration Parametric Results and Discussion

The apparatus and procedures utilized in the development of a ferrous ion oxidation process employing air or oxygen for the regeneration of coal leacher spent ferric sulfate solutions were described in detail previously (Subsection 3.2.3.2.3). Table 24 (page 66) lists the major parameters investigated and Table 23 (page 65) summarizes all the data generated during the reagent regeneration investigations.

Initial studies involved scanning of parametric effects anticipated as important to this unit operation. The starting solutions were spent ferric sulfate reagents from extraction of Lower Kittanning coal samples to which small amounts of iron sulfate were added, if necessary, to obtain the desired ferrous to ferric ion ratio (nominally 5 wt% Fe solution consisting of 30% Fe^{+2} and 70% Fe^{+3}). The generated data is summarized in Figure 15, where percent ferrous ion oxidized to ferric ion is plotted against reaction time. Each data point was computed from ferrous ion and total iron analyses of the regenerating solution and the feed concentrations of the same species. The curves in Figure 15 indicate strong dependence of ferric ion regeneration rate on temperature (Exp.R2 vs R3), oxygen partial pressure (Exp.R1 vs R2), and ferrous ion concentration or ferrous to ferric ion ratio (Exp.R2 vs R2A). The magnitude of these rate effects was determined from the data in Table 23 and is quantitatively presented in Figure 16. The indicated rate equation was selected as the one best fitting the data from a number of simple rate expressions tried. It is first order in oxygen and second order in ferrous ion. Therefore, the slopes of the curves of Figure 16 represent the product of the rate constant and oxygen concentration (the oxygen concentration remained constant throughout the reaction since the partial pressure of oxygen in the feed gas was constant and large excess of gas was used):

$$\text{Slope} = \frac{\left(\frac{1}{Fe^{+2}}\right)_2 - \left(\frac{1}{Fe^{+2}}\right)_1}{t_2 - t_1} = \frac{\Delta\left(\frac{1}{Fe^{+2}}\right)}{\Delta t} .$$

$$\lim_{\Delta t \to 0} \frac{\Delta\left(\frac{1}{Fe^{+2}}\right)}{\Delta t} = \frac{d\left(\frac{1}{Fe^{+2}}\right)}{dt} = - \frac{\frac{dFe^{+2}}{[Fe^{+2}]^2}}{dt} = k_R[O_2]$$

Comparison of slopes shows that a 90° increase in temperature increased the rate approximately sixfold and that substitution of oxygen for air

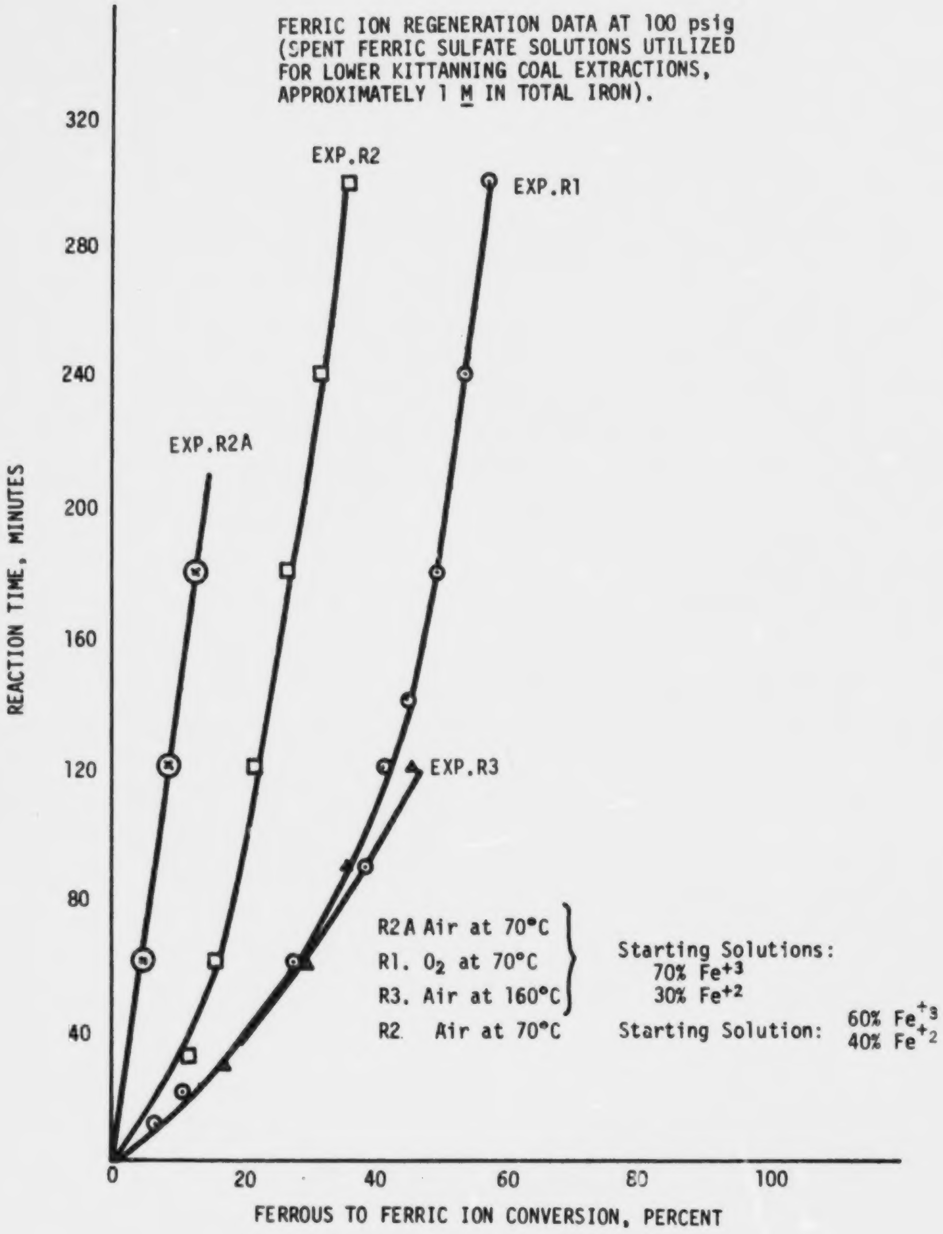


FIGURE 15. FERRIC ION REGENERATION RATES

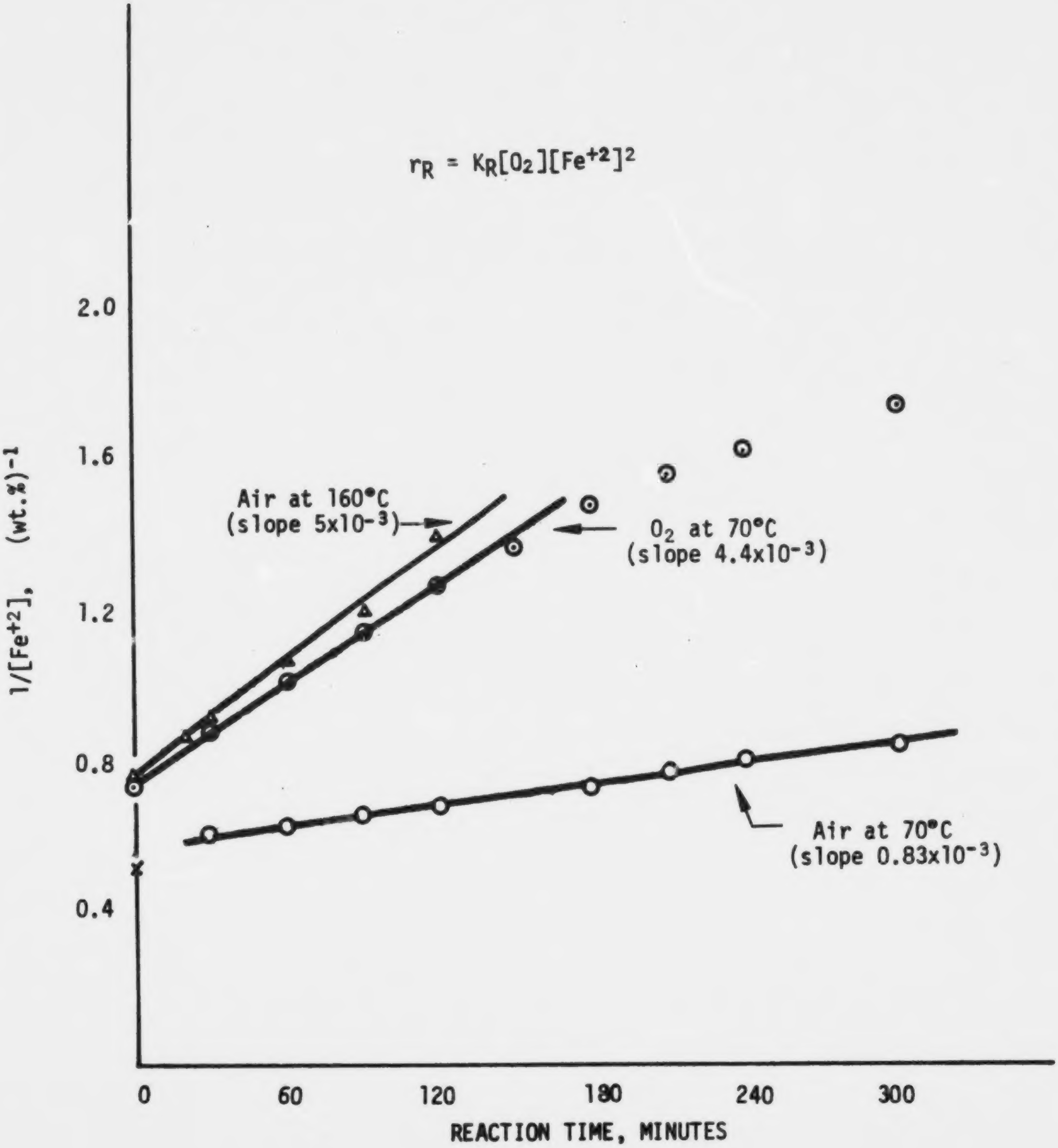


FIGURE 16. EFFECT OF TEMPERATURE AND OXYGEN PARTIAL PRESSURE ON FERRIC ION REGENERATION

increased the isothermal rate by a factor of approximately five as would be expected from an efficient aerator.

This preliminary experimental parameter effect study of ferric ion regeneration was expanded from the 4 experiments shown above to all 39 regeneration experiments in order to test the validity of the above conclusions and to investigate additional effects such as total iron concentration, liquid and gas flowrates, and apparatus geometric effects on the rate of regeneration. The findings and deductions are summarized in the ensuing paragraphs:

- The effects of major parameter variations on ferric ion regeneration are depicted in Figure 17. The figure presents the data obtained from eight experiments performed under a spectrum of experimental variables. All starting solutions were 5 wt% in total iron (spent ferric sulfate) consisting of 30% Fe^{+2} and 70% Fe^{+3}. The data is plotted as reciprocal ferrous ion concentration vs regenerator reaction time. Thus, the obtained linear curves indicate that

$$\frac{d\left(\frac{1}{Fe^{+2}}\right)}{dt} = \text{constant} \qquad (13)$$

  for a given reaction temperature and pressure, oxidant gas (air or oxygen) and liquid flowrate.
  Equation (13) shows that in all cases the regenerator reaction rate is second order with respect to ferrous ion concentration, or

$$r_R = -\left(\frac{d\ Fe^{+2}}{dt}\right)_{\text{Gas},T,P,Fe^{+2}/Fe^{+3},\ \text{Fe},\text{Liq.flowrate}}$$

$$= \text{constant} \times (Fe^{+2})^2 \qquad (14)$$

- The effects of Fe^{+2}/Fe^{+3} ratio and total iron concentration at various reaction temperatures and pressures, oxidant gases and liquid flowrates were investigated in Experiments R6 and R21 through R32 (see Tables 23 and 24). These experiments were performed with starting solutions varying in Fe^{+2} to Fe^{+3} ratio from 15%/85% to 100%/0.0% and total iron concentration from 3.3 to 10 wt%. The obtained data indicated that neither the Fe^{+2} to Fe^{+3} ratio nor the total iron concentration have any effect on regeneration rate provided enough oxygen is present in the reacting solution to accommodate the ferrous ion oxidation. Thus, Expression (14) becomes

$$r_R = -\left(\frac{dFe^{+2}}{dt}\right)_{\text{Gas},T,P,\text{Liq.flowrate}} = \text{constant} \times (Fe^{+2})^2 \qquad (15)$$

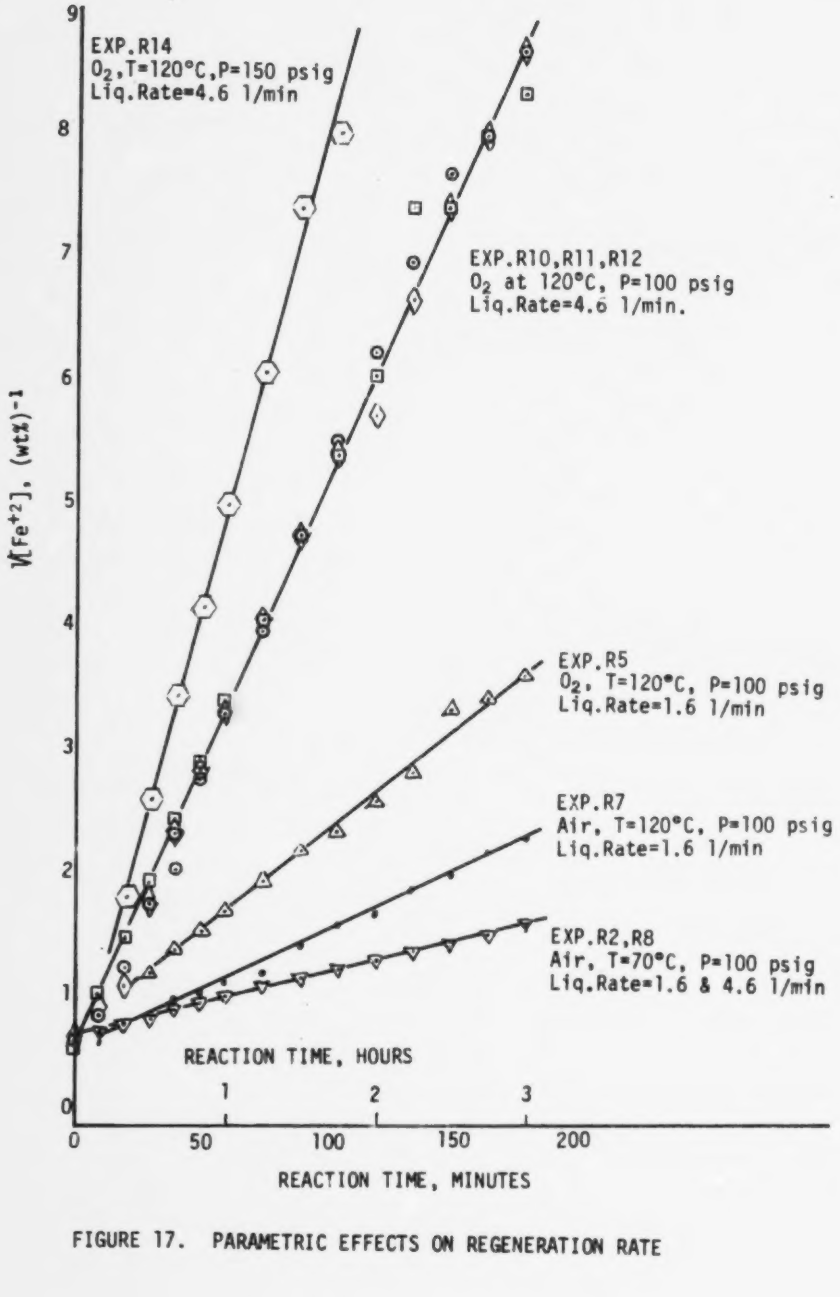


FIGURE 17. PARAMETRIC EFFECTS ON REGENERATION RATE

That is, there is no need to specify the total iron concentration and the iron forms ratio; the regeneration rate is independent of them.

- The effects of reaction pressure and type of oxidant gas (air or oxygen) on ferric ion regeneration were investigated at three reaction temperatures (70°C, 100°C and 120°C). Table 28 below illustrates these effects on rate.

TABLE 28. Effect of Oxygen Partial Pressure on Regeneration Rate

Oxidant Gas	Reaction Pressure (psig)	Reaction Temp (°C)	Liquid Flowrate (l/min)	Reaction Rate $\times 10^3$*	References
Air	100	70	4.6	1.1	R8
O_2	100	70	4.6	5.0	R9
Air	100	120	4.6	9.3	R13
O_2	100	120	4.6	46.0	R10
O_2	150	120	4.6	73.0	R14
Air	150	100	4.6	6.6	R16
O_2	150	100	4.6	31.0	R15
Air	100	70	1.6	0.9	R2
O_2	100	70	1.6	4.0	R1
Air	100	120	1.6	4.4	R7
O_2	100	120	1.6	16.0	R5

*Rate is expressed as $-d\frac{1}{Fe^{+2}}/dt$ in order to eliminate the ferrous ion concentration effect; Fe^{+2} is in wt% of solution and t in minutes (refer to Table 23 for data used in rate computation).

The first horizontal section of this table compares air and oxygen data obtained at 70°C; the difference in rates is approximately that expected from the difference in oxygen partial pressure (a factor of 5). The first two entries of the next section verify the factor of five difference (100% oxygen vs 21% oxygen in air). Comparison of the rates in 2nd and 3rd row of Section 2 (R10 vs R14) indicates that 50% increase in total pressure (oxygen pressure) increases the regeneration rate by nearly the same percentage. Data at 150 psig and 100°C (third table section) shows an identical relationship between oxygen and air regeneration results. Thus, the rate of ferric ion regeneration is proportional to oxygen partial pressure and Expression (15) becomes

$$r_R = -\left(\frac{dFe^{+2}}{dt}\right)_{T,\text{liquid flowrate}} = K_R(O_2)(Fe^{+2})^2 \qquad (16)$$

- The last two sections of Table 28 present data similar to that of the first and second sections but at 1.6 liter per minute solution flowrate. It is seen that the ratio of oxygen to air reaction rate in the regenerator is less than 5 and decreases with increasing temperature (or regeneration rate). In Section 3.2.3.2.3 where the regeneration apparatus and procedures were described, the dependence of the rate constant on liquid flowrate was indicated and discussed. It was characterized as a geometric effect (liquid-gas mixing problem) and it was pointed out that as the regeneration rate increases, either because of temperature or ferrous ion concentration increase, the geometric effect on ferrous ion oxidation becomes more severe. The same rate behavior was observed when the "holding tank" in the regeneration apparatus was enlarged. Separation of gas and liquid occurs in the tank and an increase of liquid flowrate proportional to tank enlargement did not correct the mixing problem.

  Figure 18 illustrates the geometric effects on reaction rate. The ordinate of the plot shows both ferric ion percentage of the total iron present in the spent solution and normalized reciprocal ferrous ion concentration; the abcissa represents regeneration reaction time. Thus, the slopes of the curves should be constant according to eq 15 and equal to the product $K_R(O_2)$; the oxygen partial pressure was the same for all experiments. Since the slopes of the three curves are not constant, the liquid flowrate and size of holding tank are not true variables of the regeneration rate, but represent apparatus geometric limits which should be considered in the unit's design. It is apparent from Figure 18 that once ferric ion regeneration reaches 85% (from 70% to 95-96% of total iron in solution) the three slopes become identical and the regeneration rate obeys Experession (16). The above discussion pointed out that the ferric ion regeneration rate can be confidently expressed by

$$r_R = -\frac{dFe^{+2}}{dt} = K_R(O_2)(Fe^{+2})^2 \qquad (17)$$

  where K_R depends only on temperature, provided regeneration geometric parameters (holding tank and loop length or pumping rate) are not permitted to cause liquid-gas separation. Units of eq (17) were defined in Section 3.2.3.2.3.

- The data presented in Tables 23, 24 and 28 indicate that the dependence of K_R on temperature was thoroughly investigated in the range of 70°C to 120°C (experiments at 160°C were also conducted, but oxidation of the utilized apparatus

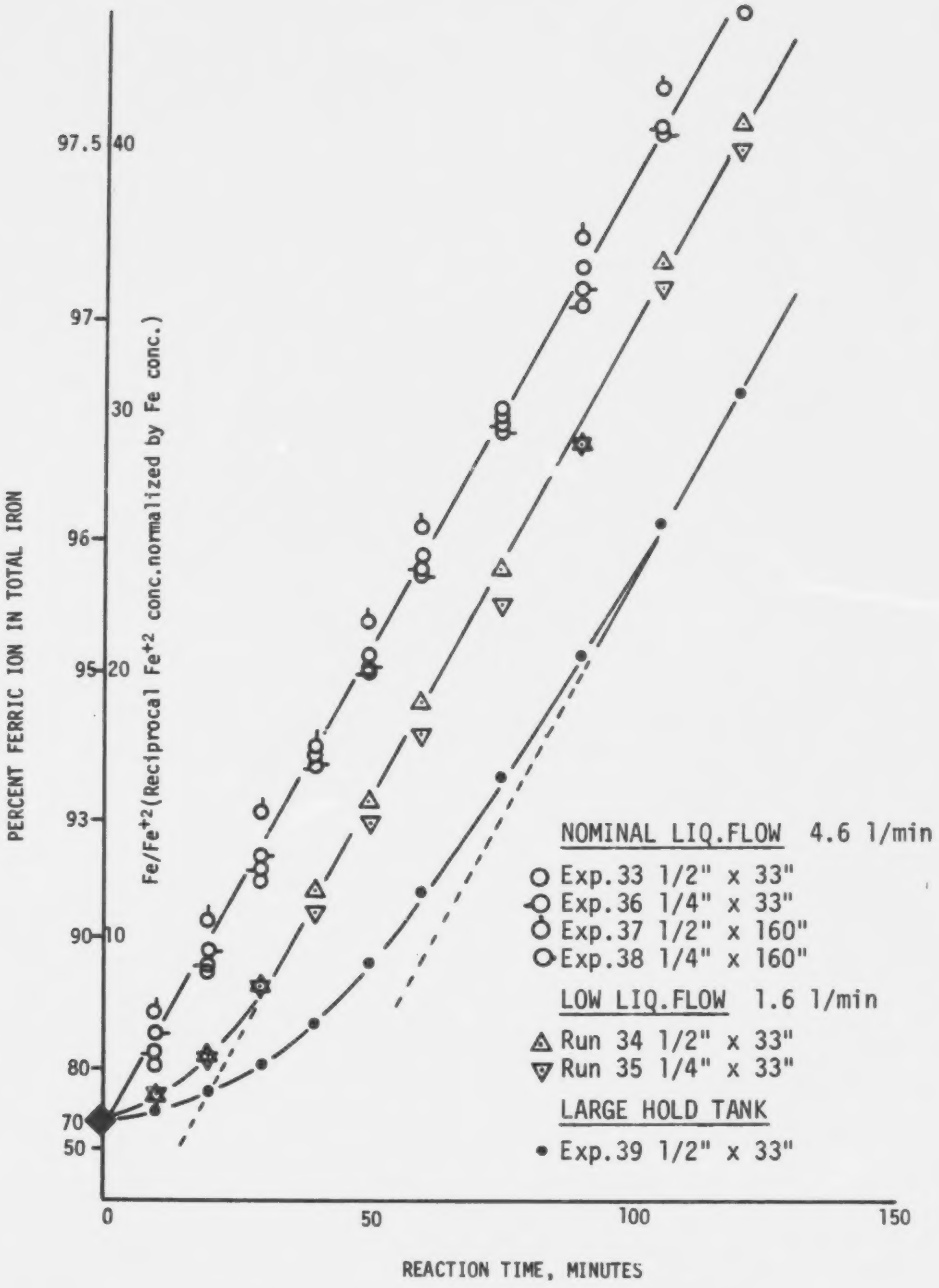


FIGURE 18. GEOMETRIC EFFECTS OF REGENERATION RATE

rendered the results questionable). Analysis of the data showed that the dependence of K_R on temperature can be well represented by the Arrhenius equation:

$$K_R = A_R \exp(-E_R/RT) \tag{18}$$

where

$$A_R = 6.7 \times 10^5 \text{ liters/mole-atm-min}$$

and

$$E = 13.2 \text{ Kcal/mole}$$

Expressions (17) and (18), together with the data on liquid-gas mixing (geometric effects), represent the necessary information for the design of the *ex situ* spent ferric solution regeneration unit for the pyritic sulfur removal process. The measured regeneration rates are the most efficient obtainable from the chemistry of the process (uncatalyzed). Furthermore, these rates are more than adequate to accommodate the generation of ferrous ion in the leacher. That is, the ferric ion regeneration rate is substantially faster than the overall pyritic sulfur leaching rate obtained to date.

3.2.3.3.9 Process Improvement Probing Experiments

Six experiments were performed during the last stages of the program in order to probe possible process improvements suggested by the data or dictated by process economics. They dealt with

- Elemental sulfur recovery prior to washing spent ferric salts from coal,
- Coal leaching under pressure for pyritic sulfur removal,
- Simultaneous coal leaching and reagent regeneration.

The elemental sulfur recovery prior to coal washing experiments proved very successful. The elemental sulfur recovered from toluene extraction was that expected from the attained pyrite extraction by assuming a sulfate to sulfur ratio of 1.5 to 1. In addition, the iron content of the processed coal and its residual sulfate indicated that coal washing in the presence of toluene is efficient. In these experiments the coal/iron sulfate slurry from the leacher was filtered and the wet coal extracted with toluene at reflux temperature for one hour. The spent toluene was separated from the extracted coal by filtration; it was then distilled to yield a water-toluene distillate and a residue consisting principally of elemental sulfur. The toluene wet coal was washed with 90°C water and dried. Even though additional work is required for firm conclusions, this procedure may be very desirable in commercial scale plants. The advantage in the reversal of unit operations results from reduced coal drying requirements. Toluene from elemental sulfur extraction may be displaced from the coal by water, and this would alleviate the necessity for complete drying of the coal, or even drying it at all.

Another set of process improvement experiments involved pyritic sulfur leaching under N_2 at 150 psig in a batch mode. Two coal particle sizes were investigated: -1/4 inch by +10 mesh and -100 mesh. Leaching temperatures of 120°C and 140°C were used with the first coal size while 130°C was used with the -100 mesh coal. Details on the experimental conditions used and the data generated are presented in Tables B-3 and B-10 respectively, of Appendix B (Experiments 61, 62 and 63). The pyritic sulfur removals obtained with the large size coal samples after 4 hours of extraction at both temperatures with ferric sulfate were not favorable. Pyritic sulfur removals were only approximately 20%, indicating the possibility of a diffusion controlled rate (very small temperature effect). However, since there is no available data for the extraction of the same size fraction coal at ambient pressures, final conclusions on the effect of pressure (temperature) on this size coal must await further experimentation. The closest comparison that can be made is with 1/4 inch top size coal (-1/4 by 0); this coal, after 4 hours extraction at 102°C, indicated pyrite removals in the 40% range. The results of Experiment 63 (-100 mesh, 4 hours, 130°C) were very promising. Pyrite removal was 81% vs 60% to 65% for ambient pressure, 102°C, and 4 hour extraction of the same size coal. Thus,a 30°C increase in temperature substantially increased the rate.

Even more exciting were the results from an experiment performed under simultaneous pyrite leaching-reagent regeneration conditions (Experiment 64). Pyritic sulfur removal of 84% was obtained in a 2 hour extraction of -100 mesh Lower Kittanning coal at 130°C with ferric sulfate. This removal represents a five-fold increase in average leaching rate over that obtained in 2 hours with the same coal at 102°C and ambient pressure. (Similar pyrite removal, 84%, in Experiments 50 and 56 required 9.5 and 11 hours reaction time, respectively.

Furthermore, determination of the heat content of the processed coal did not indicate perceptible oxidation. Although single experiments are not sufficient for accurate evaluations of potential process improvements, results from Experiments 63 and 64 indicate very promising approaches for improved pyritic sulfur removal process operation.

Pyritic sulfur leaching rate values were not computed for Experiment 64 because the simultaneous leaching and ferric ion regeneration operations did not permit a valid determination of ferrous ion production as a function of time. The rate values computed for Experiment 63 are erroneous because of the unexpected formation of insoluble iron compounds which deposited on the coal during leaching (formed also during Exp.64). Since rates are determined from iron forms analysis of the solution (ferric ion consumed and ferrous ion produced), the computed rates and predicted sulfur removal from iron analysis were low (see Tables 22 and B-10). These insoluble forms of iron remained on the coal after normal washing as the higher sulfate content of the processed coal indicates. The ash values of the processed coal are too high and heat content values too low, also. The processed coal from Experiment 63 was analyzed for iron and found to contain 4.64 wt%, while only 0.59 wt% would be expected from the concentration of the residual pyrite. The excess iron on the coal could not totally be justified by the additional sulfate present; about one third of it had to be in another form (probably as oxide). The coal washing procedure was modified in order to remove the residual sulfate from the coal and obtain an understanding of the nature of the insolubles.

The processed coal was riffled into two samples. One sample was washed with hot water (two stages) and the spent water was analyzed for iron forms; the iron found was in the ferrous form and accounted for approximately one half of the residual sulfate on the coal. The second sample was washed by dilute sulfuric acid (1N) followed by hot water wash (two stages). Both ferrous and ferric forms of iron were found in the spent wash solution and accounted for 95% of the excess iron in the coal. The quantity of ferrous ion in the spent wash solutions was equivalent to the residual sulfate initially found on the coal. Analysis of the washed coal indicated normal sulfate concentration (0.13 wt%). The ferric ion found in the spent wash solutions was apparently deposited on the coal as iron oxide. It is assumed that iron oxide formed from iron salt hydrolysis and that the insoluble sulfate formed because of the peculiar solubility behavior of this iron salt with temperature. Ferrous sulfate acquires a negative solubility coefficient at high temperatures; that is, while at low temperatures solubility increases with increasing temperature at high temperatures it decreases. The exact temperature of solubility coefficient reversal depends on salt concentration and solution pH. It is speculated that the degree of salt hydration changes at the coefficient reversal temperature. Empirical solubility data with spent ferric sulfate solutions from coal extractions is required for identification of the formed insoluble iron salts. Preliminary experimentation indicated that the insoluble form of iron sulfate dissolved upon mixture cooling. Thus, the excess sulfate found on the processed coal could either be removed by a modified washing procedure or by slow cooling of the high temperature slurry from the leacher.

The processed coal of Experiment 64 was not washed by the above procedure, but it is certain that the excess sulfate found on this coal could be completely removed by dilute sulfuric acid or possibly cooling of the leacher slurry.

The insoluble compounds on the coal are at least partially responsible (dilution effect) for the low heat content values indicated for processed coal from Experiments 63 and 64 (Table 22). For example, correction for the dilution effect due to iron insolubles brings the heat content of the processed coal under Experiment 64 to approximately 12,800 btu per pound, which is the expected value for the indicated pyritic sulfur removal. The same correction applied to the coal from Experiment 63 increases the btu content to only 10,500 btu per pound; this value is still too low. Since this coal was leached under nitrogen, its oxidation is highly improbable. The low heat content value may be due to analysis errors; heat content analysis was not repeated due to lack of additional sample.

3.2.4 Process Design

Process design studies for chemical removal of pyritic sulfur from coal have indicated that the process may be laid out using a number of effective alternative processing methods. Some of the variations which have been tested and considered in preliminary engineering designs include the following:

- Air vs oxygen for regeneration
- Coal top sizes from 1/4 inch to 100 mesh
- Leaching and regeneration temperatures from 50°C up to 130°C
- Leaching and regeneration in the same vessel
- Removal of generated elemental sulfur by vaporization or solvent extraction

All of the above conditions are effective and their utilization involves economic trade-offs. Processing of the smaller coal top sizes would require batch-type pressurized leaching vessels (similar to fluid-bed coking vessels) for concurrent leaching and regeneration and thickeners for concentration of the coal slurry prior to filtration, while processing of coarser coal particles could result in utilization of kiln-type countercurrent leachers with separate leach solution regeneration. Thus, the process may be amenable to incorporation of a variety of state-of-the-art process equipment.

The process design selected for detailed evaluation in this program involves three principal processing sections:

- Reactor - leaching the coal to form water soluble salts and elemental sulfur from the pyrite and regenerating the leach solution.
- Extractor - dissolving the elemental sulfur into an organic solvent.
- Washer - removing the water soluble salts from the leached, low-sulfur coal.

Each of these sections contains a number of processing steps and in addition, auxiliary sections such as grinding and drying may be required under some circumstances. A conceptual process design was prepared based on 100 tons per hour of coal feed (dry basis). The coal is assumed to have 3.2% pyritic sulfur and to consume a negligible amount of ferric ion in oxidative side reactions. This baseline case is similar to conditions which would exist when processing Lower Kittanning coal.

The following sections present the basic design data, the reactor trade-off studies, and the resultant baseline process design.

3.2.4.1 Design Data Package

The reaction section has four main process requirements which are:

- Providing mixing and wetting of ground -100 mesh coal with the aqueous ferric sulfate leach solution and raising the slurry to the operating temperature and pressure.
- Providing the residence time and reaction conditions which remove a nominal 95% of the pyrite originally contained in feed coal.
- Providing the residence time and reaction conditions which regenerate the ferric sulfate solution from the spent ferrous sulfate leach solution.
- Providing for separation of the coal from the bulk leach solution and for the separation of iron sulfate produced in the leach reaction from the recycled leach solution.

The extraction section has four main process requirements which are:

- Providing for contact of a water-immissible solvent for sulfur with the coal containing residual leach solution in order to remove the elemental sulfur from the coal and simultaneously displace a portion of the aqueous leach solution from the coal.
- Providing for separation of coal from the sulfur-rich solvent and for separation of sulfur-rich solvent from displaced leach solution.
- Providing for the recovery of elemental sulfur from the sulfur-rich solvent and recycle a sulfur-lean solvent to the contactor.
- Providing for clean-up of the sulfur by melting and hot gas or steam stripping.

The washing section has three main process requirements which are:

- Providing for contact of the sulfur-solvent-wet coal with a minimum quantity of wash water to remove water soluble iron sulfates and to displace a portion of the organic solvent from the coal.
- Providing for separation of coal from the wash water and for separation of the spent wash water from solvent which was displaced from the coal.
- Providing for vaporization of residual solvent and excess water from the processed, low sulfur coal.

Mixing - bench-scale experience indicated that up to 15 minutes of mixing may be required to wet the coal and to provide a well mixed slurry when dry, -100 mesh coal is fed. If the coal is obtained from wet grinding, or is in a pre-wetted form, less mixing time would be required.

Heating - the heat capacity of the leach solution is about the same as water and no volatile constituents are present other than water. In some cases, traces of the organic solvent used to extract elemental sulfur may be dissolved in the aqueous solution. The heat capacity was assumed to be 1.0 btu/lb °F for the leach solution and 0.3 btu/lb °F for the coal.

Leach Reaction - the net overall reaction between pyrite and the ferric sulfate leach solution is represented by:

$$FeS_2 + 4.6\ Fe_2(SO_4)_3 + 4.8\ H_2O \longrightarrow 10.2\ FeSO_4 + 4.8\ H_2SO_4 + 0.8S$$

$$\Delta H = -55 \text{ Kcal/g-mole } FeS_2 = -0.10 \text{ MM btu/lb-mole } FeS_2 \text{ reacted}$$

The reaction rate was found to have a second order dependence on both the fraction of pyrite (or pyritic sulfur) in the coal and the fraction of the total iron in the leach solution which is in the ferric ion form. The leach rate at about 212°F is as follows:

$$r_L = \frac{-d[Wp]}{dt} = K_L\,[Wp]^2\,[Y]^2$$

where:

$[Wp]$ = wt% pyrite in dry coal at time t

$[Y]$ = fraction of iron as ferric ion at time t

K_L = 0.15 when t is in hours

It is likely that the constant K_L increases with temperature, but since experimental data at higher temperatures are very limited, K_L was assumed to have the same value even at more elevated temperatures. K_L is constant with total iron concentration at least in the immediate vicinity of the nominal 5% solution chosen. Physical considerations such as increased solution density and viscosity and the limited solubility of ferrous sulfate in the ferric sulfate solution become increasingly important to the design of the pyrite leacher when total iron concentration approaches 10%.

Regeneration - the leach reaction produces both ferrous sulfate and sulfuric acid which must be processed for recycle operation. For each mole of pyrite reacted 9.6 moles of ferrous sulfate must be regenerated to maintain the acid at a constant level.

$$9.6\ FeSO_4 + 4.8\ H_2SO_4 + 2.4\ O_2 \rightarrow 4.8\ Fe_2(SO_4)_3 + 4.8\ H_2O$$

$$\Delta H = -18.6 \text{ Kcal/g-mole } FeSO_4 = -.0335 \text{ MM btu/lb-mole } FeSO_4$$

$$= -.34 \text{ MM btu/lb-mole } FeS_2 \text{ reacted}$$

If hydrolysis of a portion of the ferric sulfate to iron oxide should occur:

$$Fe_2(SO_4)_3 + 3\ H_2O \longrightarrow Fe_2O_3 + H_2SO_4$$

then additional regeneration of ferrous ion would be required to remove the acidity produced from the hydrolysis reaction. The extent of hydrolysis at temperatures below 250°F appears to be negligible, but at higher temperatures there is evidence of ferric oxide and possibly a low hydrate or anhydrous ferrous sulfate precipitation. The hydrolysis products and/or precipitates formed at 265°F were found to redissolve slowly in ambient temperature spent leach solution and do not remain as permanent products. No data was obtained above 265°F.

The regeneration rate was found to be second order in the molar concentration of ferrous ion over the range of ferrous concentration from 100% to less than 1% of the total iron. The rate is

$$r_R = \frac{-d[Fe^{+2}]}{dt} = K_R\ [Fe^{+2}]^2\ [O_2]$$

where:

$[Fe^{+2}]$ = concentration of ferrous ion, mole/liter
$[O_2]$ = oxygen partial pressure, atm
K_R = 1.836 liters/mole-atm-hour at 248°F

Over the range of temperatures studied (212°F to 265°F) the rate constant was found to vary exponentially with temperature.

$$K_R = 40.2 * 10^6 \exp(-13{,}200/RT)$$

which gives:

Temp., °F (°C)	K_R, liters/mole-atm-hour
212 (100)	0.74
230 (110)	1.18
248 (120)	1.84
266 (130)	2.79

The ferric sulfate regeneration rates were obtained under conditions where oxygen in the form of minute air or oxygen bubbles was dispersed throughout the ferrous sulfate solution. Thus, all of the solution was continually saturated with oxygen at the partial pressure of oxygen present in the regeneration gas. At bench-scale, the minute bubbles were formed by pumping a portion of the liquid in turbulent flow (N_{Re} >3000) through a pipe whose length was 50 or more times its diameter. Gas containing oxygen was added to the liquid in an amount ranging from less than 1% to greater than 10% by volume at flow conditions. The method is very similar to aeration equipment used to reduce the biological or chemical oxygen demand of chemical plant effluent streams, except that ferric sulfate regeneration is conducted at more elevated temperatures and pressures.

Separation - the major separation step requires treated, -100 mesh coal to be separated from the spent leach solution. The four principal methods which could be employed are hydrocyclones, centrifuges, filters and thickeners. The -100 mesh coal is about 10% to 15% (w/w) above 100 microns in diameter and 10% (w/w) below 20 to 40 microns in diameter. Hydrocyclones are not useful for particle sizes below several hundred microns and centrifuges would require very high input and recycle rates to separate the coal from the leach solution because of the fine particle size and the small liquid-solid density difference. Filtration is applicable, but for slurries less than 30 or 35% solids, the filter area requirements are very large. Typically, a 10% solids slurry needs almost two orders of magnitude more filter area than a 35 to 55% slurry. Thickeners have been used on commercial scale to remove coal fines from water and other aqueous media. Data for similar density solutions and coal sizes were obtained from a thickener manufacturer. It is estimated that a thickener area of about 20 ft^2 per ton/day of coal with an edge depth of about 8 feet will provide an underflow with greater than 35% solids and an overflow containing only few tenths percent (or less) solids when the feed contains 10 to 20% solids. Since the thickener slurry can be maintained near the leach solution boiling point, the time spent in the thickener can be used to carry the leaching reaction to greater degree of completion and to redissolve any solids formed during regeneration.

Iron sulfate removal - during the leaching of pyrite from coal the pyrite adds both iron and sulfate to the leach solution. For each mole of pyrite reacted, it is necessary to remove 1.0 mole of iron and 1.2 moles of sulfate from the solution. If regeneration is established at the level where constant acidity is maintained, then iron sulfates can be removed as a mixture of ferrous and ferric sulfate as follows:

$$1.0 \text{ mole } FeS_2 \longrightarrow \begin{matrix} 0.2 \text{ moles } Fe_2(SO_4)_3 \cdot xH_2O \\ 0.6 \text{ moles } FeSO_4 \cdot y\, H_2O \end{matrix}$$

The ferrous sulfate could also be recovered as basic ferric sulfate:

$$0.6\ FeSO_4 + 0.3\ H_2O + 0.15\ [O_2] \longrightarrow 0.6\ Fe(OH)SO_4$$

It is obvious that iron must be removed from the solution in the ratio of 0.4 moles of Fe^{+3} to 0.6 moles of Fe^{+2}. The leach solution, however, is maintained at high Fe^{+3} levels (typically above 0.7 Fe^{+3} to 0.3 Fe^{+2}). Nonselective removal of a portion of the leach solution would lead to a depletion of sulfate (if the correct amount of iron were removed) or a buildup of iron (if the correct amount of sulfate were removed). Fortunately, ferrous sulfate can be preferentially removed from the solution in any of several ways. For example, if the solution temperature is raised an anhydrous or low hydrate ferrous sulfate is precipitated which redissolves in a cooled solution slowly enough that separation can be accomplished. A second procedure involves concentrating a portion of the spent solution to about a 50% salt concentration and cooling to crystallize the hydrous ferrous sulfate. Maximum solubility occurs at about 150°F. At room temperature it was found that a solution containing 5% Fe^{+3} would dissolve only about 3% Fe^{+2}. Concentrations above about 8% iron will preferentially precipitate ferrous sulfate. This is a lower salt concentration than reported in the literature.

Filtration - the thickener underflow which contains a minimum 35 wt% solids can be further "dewatered" by filtration. Commercial data shows filtration rates with either vacuum or pressure filters generally fall in the range of 70 to 400 lb/hr/ft^2. For the 35% slurry at 200°F and a solution viscosity of about 0.5 centipoise, a filtration rate of 200 lb/hr/ft^2 (dry coal basis) is expected to yield a cake with about 35 wt% residual leach solution (dry basis).

In most bench-scale experiments, the filter cake was water washed immediately following the filtration. The wash solutions were analyzed for iron from which a typical value of 35 wt% leach solution on the cake was calculated for 100 mesh top size coal. Single point data for other coal sizes gave: 42% leach solution with 200 mesh coal, 30% leach solution with 1/4 inch top size coal. A single point calculation for 100 mesh coal with an 11% total iron leach solution showed 42% retention of leach solution on the filter cake.

Separation of coal from a slurry composed of 33% solids and containing organic solvent would have a rate of about 400 lb/hr/ft^2 and is expected to give a cake with 25 wt% liquid (5% residual leach solution and 20% solvent). Two bench-scale experiments were conducted with organic solvent extraction of the leach solution wet filter cake. These tests verified complete removal of elemental sulfur, but measurement of the organic solvent/aqueous solution ratio was not attempted. The 5%/20% ratio is an estimate which is best verified at pilot scale in commercial type filtration equipment.

Separation of coal from the hot wash water at a filtration rate of 200 lb/hr/ft^2 is expected to give a product with 30% liquid (25% water and 5% solvent). Two bench-scale experiments, in which organic extraction of sulfur preceded water washing, resulted in slightly lower (but within experimental variation) values of residual sulfate on the processed coal when compared to experiments in which the coal was washed first. The purpose of these experiments, as mentioned above, was to verify complete sulfur removal and no data were obtained for the water/solvent ratio on the washed coal. The water/solvent ratio is expected to depend more on the extent of mixing and skimming prior to filtration than on the filtration equipment.

Filtration of precipitated sulfur from the circulating solvent involves clarifying the solvent stream containing about 0.5 wt% solid sulfur. Filtration rates will be highly dependent upon the particle size and shape. Based on separation of submicron particles from lubricating oils it is estimated that filtration rates of about 50 gal/hr/ft^2 will be obtained.

A filter also is required to separate the iron sulfate crystals from a portion of the spent leach solution. Since the solids may contain small amounts of hydrous iron oxide, a low filtration rate of 50 $lb/hr/ft^2$ was chosen for slurries above 35 wt% solids, and a rate of 1 $lb/hr/ft^2$ for each percent of total solids was selected for slurries below 25 wt% solids.

3.2.4.2 Optimization of Process Design

In the design of a process for removing pyritic sulfur from fine sized coal, it is not feasible to operate the reactors in a counter-current flow mode since coal particles are entrained in the liquid stream. Although in principle it is possible to separate partially spent leach solution from the coal, regenerate the solution, and return it, in practice, the filtration areas become uneconomically large. For example, in order to maintain the leach solution at ferric ion ratios (Y) between 0.7 and 0.9, it is necessary to circulate an average of 26 tons of leach solution per ton of coal for complete pyrite removal from a 3.2% pyritic sulfur coal. The reactor volume would be excessive if this liquid/coal ratio were used. At a more practical liquid/coal weight ratio of 4, it would be necessary to remove and regenerate 22 tons of leach solution per ton of coal during the reaction in addition to the final separation. Since filtration of a 20 wt% coal slurry will probably have a rate equivalent to 50 to 100 $lb/hr/ft^2$, the required filter area for leaching 100 tons of coal per hour would be of the order of 50,000 to 100,000 square feet. It was concluded that fine coal is best processed in a system which leaches the pyrite and concurrently regenerates ferric sulfate without separating the slurry.

Each of the process schemes evaluated starts with a small, short residence time mixing vessel in which the coal is fully wetted with aqueous leach solution prior to entering the reaction train where oxygen is present. The reaction train in which both leaching and regeneration occur may be one or a series of flow-through reaction vessels, or the reaction train may be a group of vessels in parallel. These alternates are sketched in Fig.19.

The advantage of the flow-through reaction scheme is that each vessel operates at steady state and the processing conditions may be adjusted to more optimum levels as the coal slurry passes from vessel to vessel. The chief disadvantage is that portions of the coal have wide variations of residence on both sides of the average residence time. For example, in an ideal stirred reactor 10% of the coal has less than one tenth the average residence time and 10% has more than 2.3 times the average residence time. The highly non-linear removal of pyrite with residence time makes the flow through reactor system highly inefficient in its use of residence time. In one example calculation, a flow-through vessel with an average residence time of 10 hours had an effective residence time of less than 5 hours and produced an average 70% pyrite removal. At still higher pyrite removal, the flow-through system becomes progressively more and more inefficient.

The main reactor optimization is reduced to the selection of the best operating conditions and number of parallel batch mode vessels to accomplish the desired pyrite removal.

A model of the leaching and regeneration reactions was programmed for the computer. This program sized and costed the reactor vessels required. The vessels' costs were found to decrease with both decreasing liquid to coal weight ratio (L/C) and with increasing temperature and were found to have a minimum in the vicinity of 50 psig when oxygen was used to regenerate the solution. Typical reactor cost results are shown in Figs. 20 and 21. Since there is some experimental evidence that the leacher reaction rate constant may increase significantly with increasing temperature. Fig.21 also shows the effect of pressure at 266°F with a leacher rate constant double the nominal value.

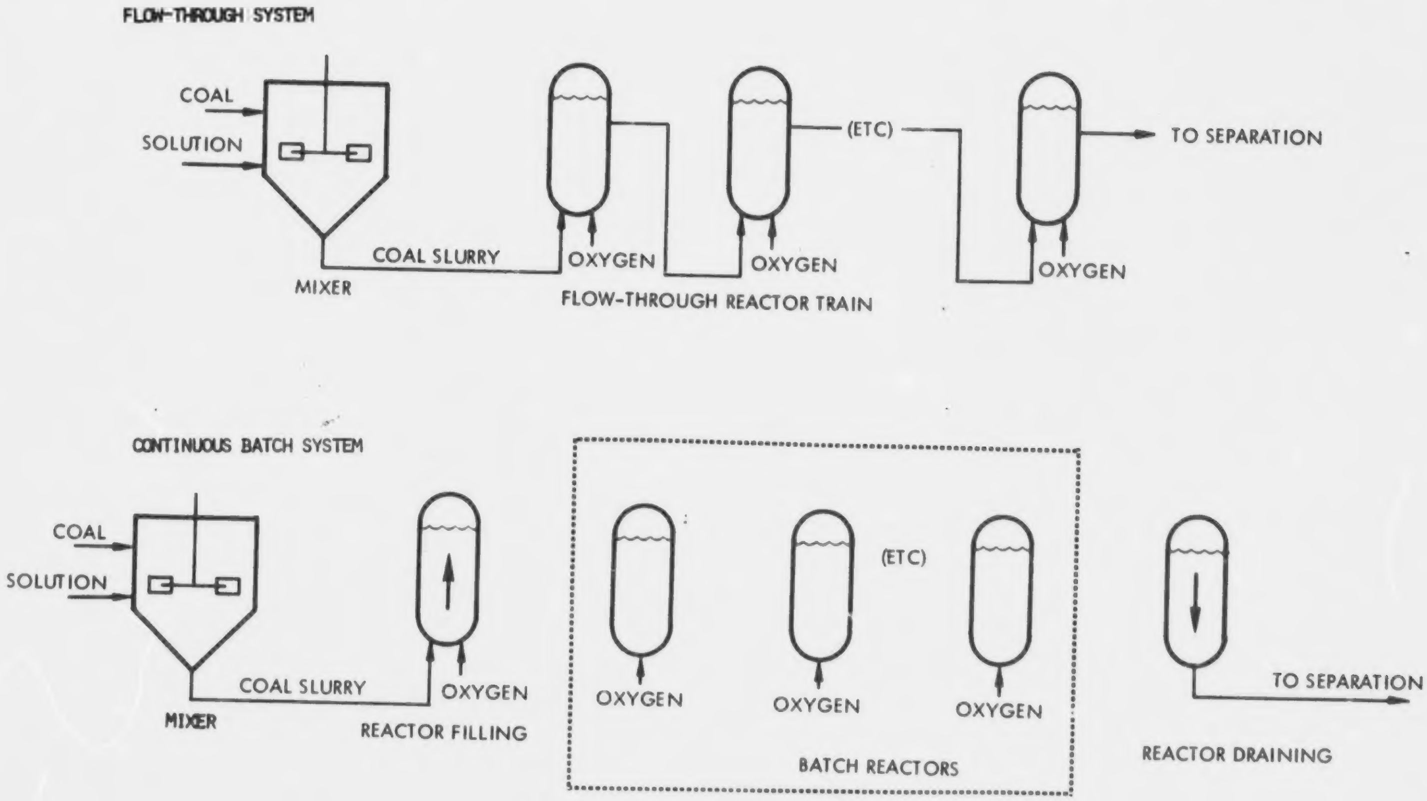

FLOW-THROUGH SYSTEM
COAL
SOLUTION
MIXER
COAL SLURRY
OXYGEN
OXYGEN
(ETC)
OXYGEN
TO SEPARATION
FLOW-THROUGH REACTOR TRAIN
CONTINUOUS BATCH SYSTEM
COAL
SOLUTION
MIXER
COAL SLURRY
OXYGEN
REACTOR FILLING
OXYGEN
OXYGEN
(ETC)
OXYGEN
BATCH REACTORS
TO SEPARATION
REACTOR DRAINING

FIGURE 19. REACTION SCHEME ALTERNATIVES

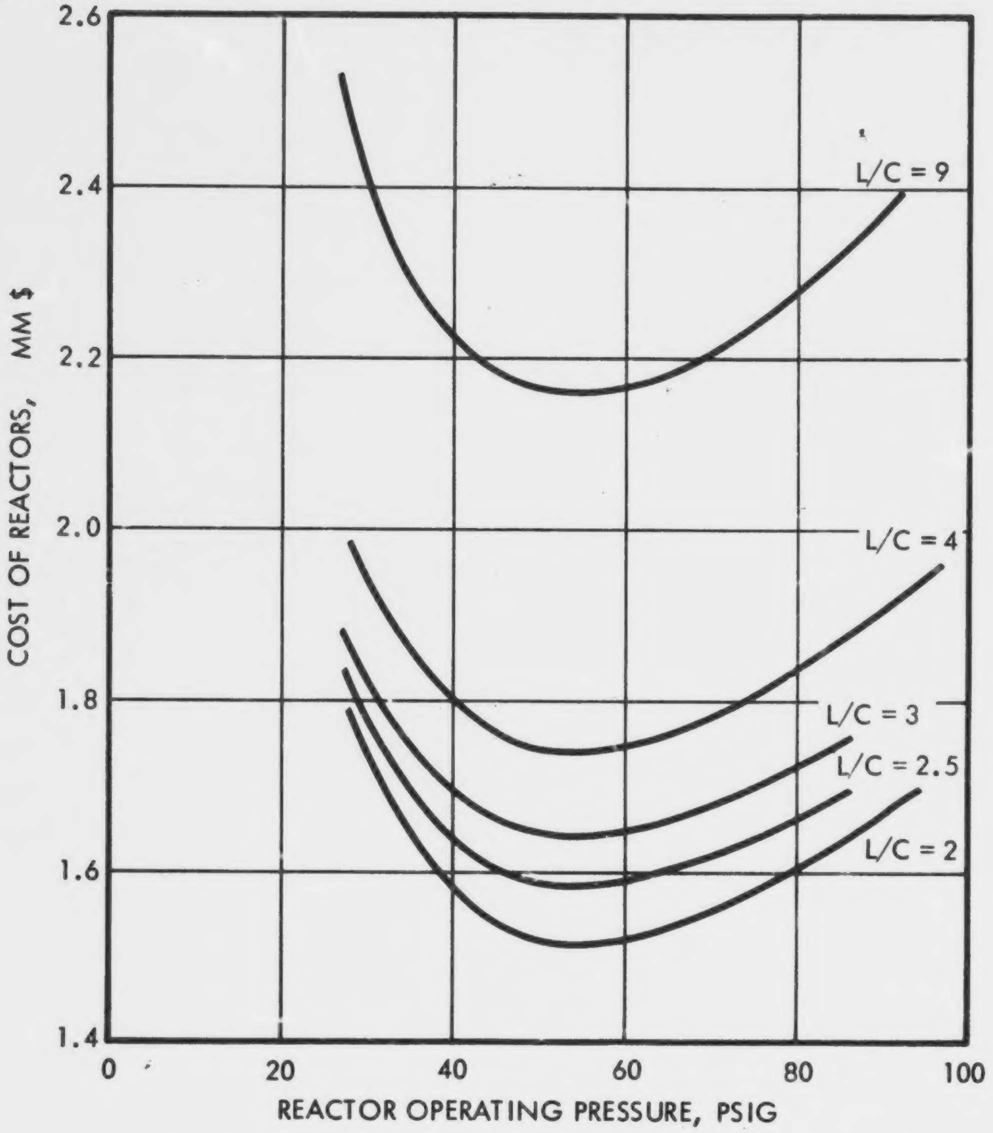


FIGURE 20. REACTOR COST FOR T = 248°F (120°C)

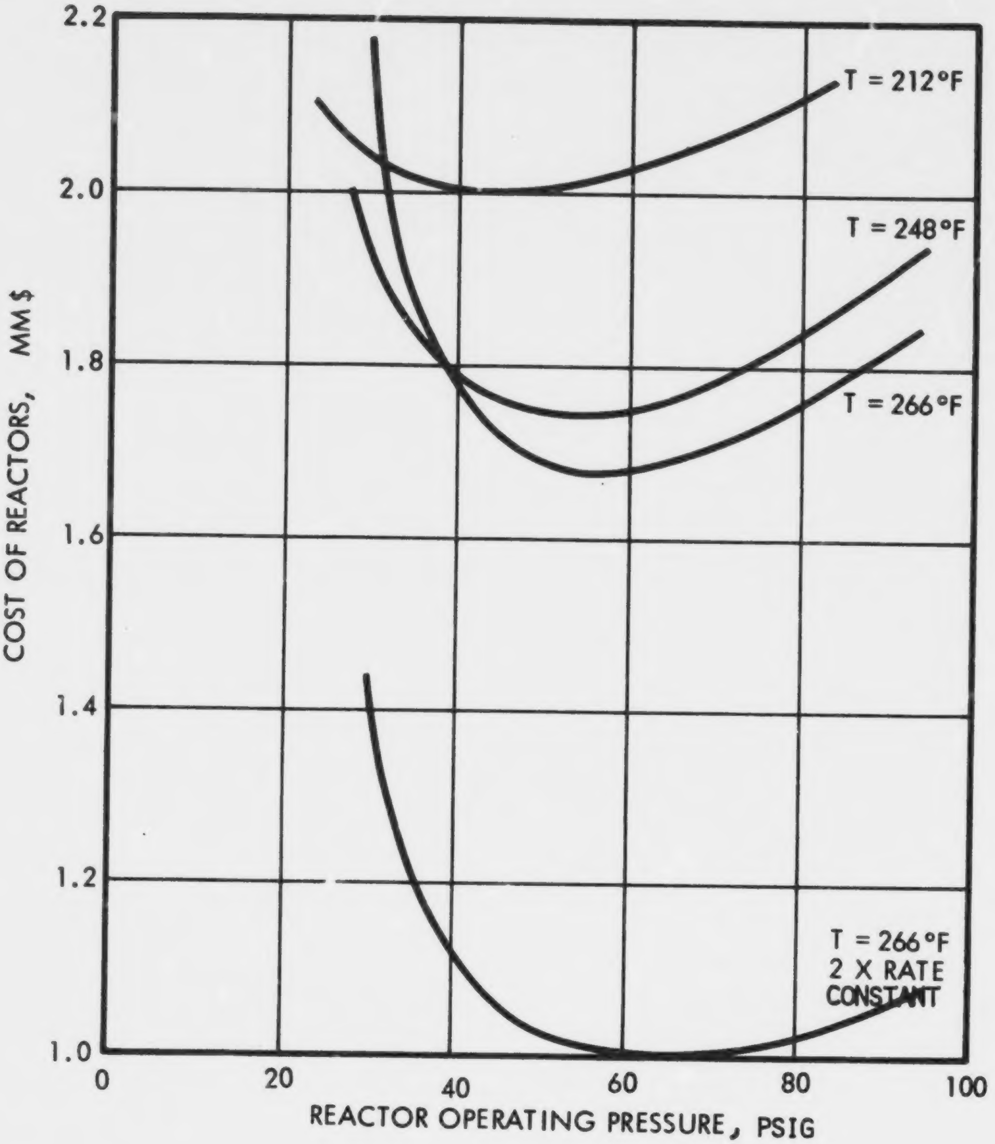


FIGURE 21. REACTOR COST FOR L/C = 4.0

The use of air rather than oxygen appears relatively unattractive. Costs using air at the same throughput and pyrite removal as the preceding reactor optimization were determined for several selected cases, but a complete optimization was not attempted. When oxygen at 99.5% purity is purchased, 2.1 million standard cubic feet per day (MMSCFD) of gas is required which would be supplied at pressures up to 300 psi at no additional cost. When air is used, the same quantity of oxygen will be consumed, but to determine the optimum quantity of air to be fed a complex trade-off study is required to compare increased process capital and operating costs with purchased oxygen costs. The major factors to be considered in the trade-off are:

- The extent of oxygen depletion from the air. At 80% depletion, 12MM SCFD of air is required, and the average oxygen partial pressure is about one-tenth of the reactor total pressure. At 20% depletion, 47 MM SCFD of air is required, and the average oxygen partial pressure is about one-fifth of the reactor pressure.
- The reactor total pressure. The rate of ferric ion regeneration is directly proportional to the oxygen partial pressure. Over the useful range of oxygen depletions, a five to ten-fold reduction in rate or increase in pressure is required. A lower regeneration rate will increase the number or size of the reactors while an increase in pressure will increase the wall thickness and cost of the reactors.
- The heat and water balance. The spent air vented from the reactor will be saturated with water vapor. The amount of water vapor depends upon the pressure and temperature of the reactors. Examples of the effect of pressure, temperature and oxygen depletion on the heat and water loss are as follows:

Reactor Temp.°F	Reactor Press.psig	Oxygen Depletion%	Water Loss T/hr	Heat Loss MM Btu/hr
212	45	80	9	18
212	45	20	35	70
212	150	80	3	5
212	150	20	10	20
248	45	80	26	53
248	45	20	103	207
248	150	80	6	12
248	150	20	25	50

As stated previously, a complete trade-off study was not attempted, but the following comparisons will indicate the magnitude of the cost increases. An oxygen system (as shown in Fig.21) has a reactor cost of nearly $1.8MM at 248°F and 45 psig and provides a residence time of nearly 8 hours. At the same pressure and temperature the air regenerated system requires about 24 hours of residence time ($5.5MM for reactors) at 80% oxygen depletion and 13 hours of residence time ($3.2MM for reactors) at 20% oxygen depletion. At the same temperature and 150 psig, the residence time was calculated to be 9 to 11 hours over the same range of oxygen depletions with reactor costs ranging from $7MM to $9MM. Similarly, at lower temperatures (212°F) and 45 psig the residence time was to be 28 hrs ($6.7MM for reactors) at 80% oxygen depletion and 20 hours ($4.8MM for reactors) at 20% oxygen depletion.

Compression for the oxygen regenerated reactor system is provided by a small recycle compressor for each reactor and a main booster compressor. These compressors total about 150 horsepower and have a combined cost of less than $0.2MM. For air regeneration, the compression cost depends on both the reactor pressure and the oxygen depletion. To provide air to the 45 psig reactors the power requirements are about 100 horsepower per MMSCFD. Thus, air compression would require additional capital of about $1.2MM for 80% oxygen depletion and $4MM for 20% oxygen depletion. The compression costs would be approximately twice as much for the 150 psig reactors.

A summary comparison of the air regeneration cost with oxygen regeneration cost is as follows:

Gas Used	O_2	Air	Air	Air	Air
Reactor pressure, psig	45	45	45	45	150
Reactor temperature, °F	248	248	248	212	248
Oxygen depletion, %	95	20	80	80	80
Reactor cost, $MM	1.8	3.2	5.5	6.7	9
Compression cost, $MM	0.2	4.0	1.2	1.2	2
Total capital, $MM	2.0	7.2	6.7	7.9	11
Annual cost, $MM/yr	0.4	1.4	1.3	1.6	2.2
Oxygen cost, $MM/yr	0.3	0	0	0	0
Total cost, $MM/yr	0.7	1.4	1.3	1.6	2.2

In this comparison costs associated with the heat loss and water loss for the air regenerated reactor system were not included since proper design will recover much of the heat and water for use in the process. There will be some additional cost associated with the recovery and additional power cost for the compression which make air regeneration even less attractive. There appears to be no condition where the increased reactor cost, compression cost and evaporation loss will make the use of air less expensive than oxygen.

3.2.4.3 Process Baseline Design

The process for removing iron pyrite from coal is shown in a block diagram in Figure 22. The steps included in the process will be briefly described and then the complete conceptual process design flowsheet will be presented and described in detail.

Reactor Section - as shown in the block diagram, ground coal is mixed with leach solution recycled from several locations in the process. The mixing is performed in a flow-through reactor with about 15 minutes of residence time. The wetted coal, which has undergone about 10% pyrite extraction at atmospheric pressure and about 215°F, is pumped to the reaction system. The reaction system carries the leach reaction to about 83% completion and regenerates the leach solution with oxygen to a point at which the iron is slightly more than 90% in the ferric form. The slurry is reduced in pressure and temperature and sent to an atmospheric pressure, covered thickener. In the thickener the reaction of pyrite continues to at least 95% completion. At the same time the coal slowly settles to the bottom of the thickener and is separated as a 35% solids underflow and a clear leach solution overflow to be recycled to the mixer. The underflow is filtered to produce a cake with about 35% retained leach solution. All or a part of the filtrate is evaporated to produce iron sulfates for removal from the process and condensate water to be used later for coal washing.

Solvent Extraction Section - the filter cake, wet with leach solution, is mixed with about twice as much weight of light naphtha (preferably a hexane-heptane mixture) at about 160°F to dissolve the elemental sulfur from the coal and at the same time to displace a portion of the aqueous leach solution from the coal. The slurry is filtered to produce a filter cake with about 20% naphtha and 5% aqueous leach solution. The filtrate is decanted to separate the leach solution from the sulfur-rich naphtha for recycle to the mixer. The naphtha is cooled to precipitate the sulfur. After filtering to remove the solid sulfur, the sulfur-lean naphtha is reheated and returned to the mixing vessel.

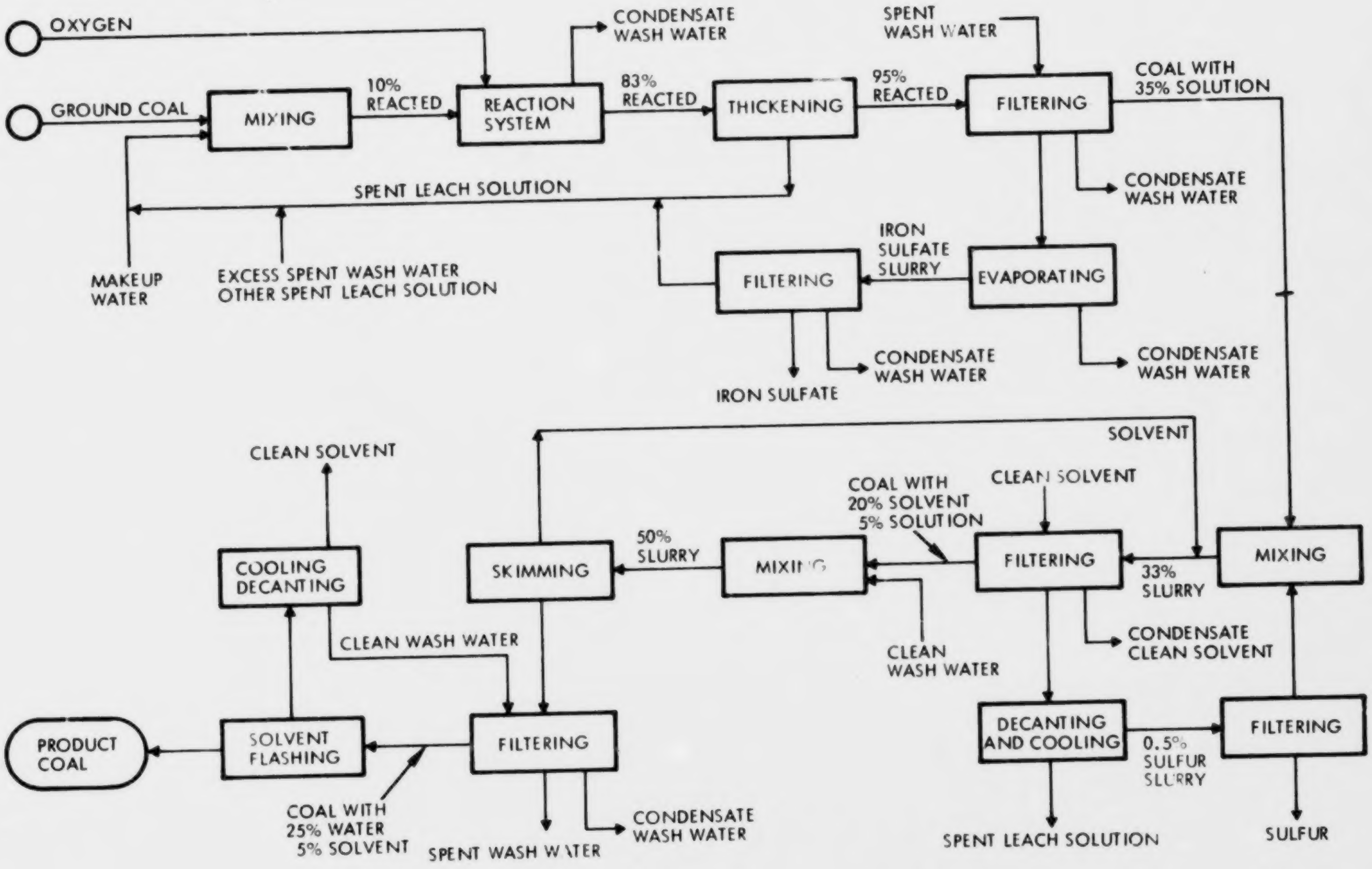

OXYGEN
GROUND COAL
MIXING
10% REACTED
REACTION SYSTEM
CONDENSATE WASH WATER
83% REACTED
THICKENING
95% REACTED
SPENT WASH WATER
FILTERING
COAL WITH 35% SOLUTION
CONDENSATE WASH WATER
SPENT LEACH SOLUTION
MAKEUP WATER
EXCESS SPENT WASH WATER
OTHER SPENT LEACH SOLUTION
IRON SULFATE SLURRY
EVAPORATING
FILTERING
IRON SULFATE
CONDENSATE WASH WATER
CONDENSATE WASH WATER
SOLVENT
CLEAN SOLVENT
COAL WITH 20% SOLVENT 5% SOLUTION
CLEAN SOLVENT
FILTERING
MIXING
33% SLURRY
CONDENSATE CLEAN SOLVENT
COOLING DECANTING
SKIMMING
50% SLURRY
MIXING
CLEAN WASH WATER
CLEAN WASH WATER
DECANTING AND COOLING
0.5% SULFUR SLURRY
FILTERING
SULFUR
SPENT LEACH SOLUTION
PRODUCT COAL
SOLVENT FLASHING
FILTERING
COAL WITH 25% WATER 5% SOLVENT
SPENT WASH WATER
CONDENSATE WASH WATER

FIGURE 22. PYRITIC SULFUR REMOVAL PROCESS BLOCK DIAGRAM

Washing Section - the filter cake from the solvent section is digested in a mixer with low salt content wash water. The denser water and coal slurry is separated from the light naphtha prior to filtering the coal from the wash water. The filter cake is coal wetted with about 25% wash water and 5% naphtha. The aqueous filtrate is partly recycled to the wash water mixer to provide a more fluid coal slurry and is partially used in the thickener underflow filter as a wash spray for the filter cake. The filter cake from the wash water filter is fed to a variable pitch screw conveyor where evaporation under vacuum recovers the solvent, some of the wash water and cools the coal to about 130°F for storage. The solvent and water vapors are recovered for recycling. A coal product is produced which is 95% free of pyrite and contains about 20% moisture.

Conceptual Process Design - the general process description and block diagram were intended to provide the overview necessary to understand the purpose of each section and operation. In this subsection, additional design considerations and details are discussed. The overall process flowsheet (somewhat simplified by omitting small pumps and vacuum filter accessories) is shown in Fig.23, and the stream mass and molar balances are given in Table 29.

Coal of 100 mesh top size (1) is blended with leach solution from the thickener (2) and recycled streams from elsewhere in the process (18). The slurry is pumped (P-1) to the mixer vessel (V-21). Steam (3) is added to raise the temperature of the slurry so that the mixer operates at the solution boiling point at atmospheric pressure. Air which was introduced with the dry coal is vented from the mixer, but no oxygen is introduced until the fully wetted coal leaves the mixer. The mixer feed rate (4) is about 1650 gpm and a 25,000 gallon mixer vessel provides the required 15 minute mixer residence time. The mixer does not operate under pressure, but the liquid head produces a pressure of about 15 psig at the mixer base.

The mixer effluent (5) is continuously pumped (P-2) to one of the reactor vessels (V-1). The pump must operate against the differential head in the reactor (30 psi when full), the oxygen pressure and the aqueous solution vapor pressure (maximum total feed pressure about 60 psig). Oxygen (1450 SCFM) for leach solution regeneration is introduced (6) into

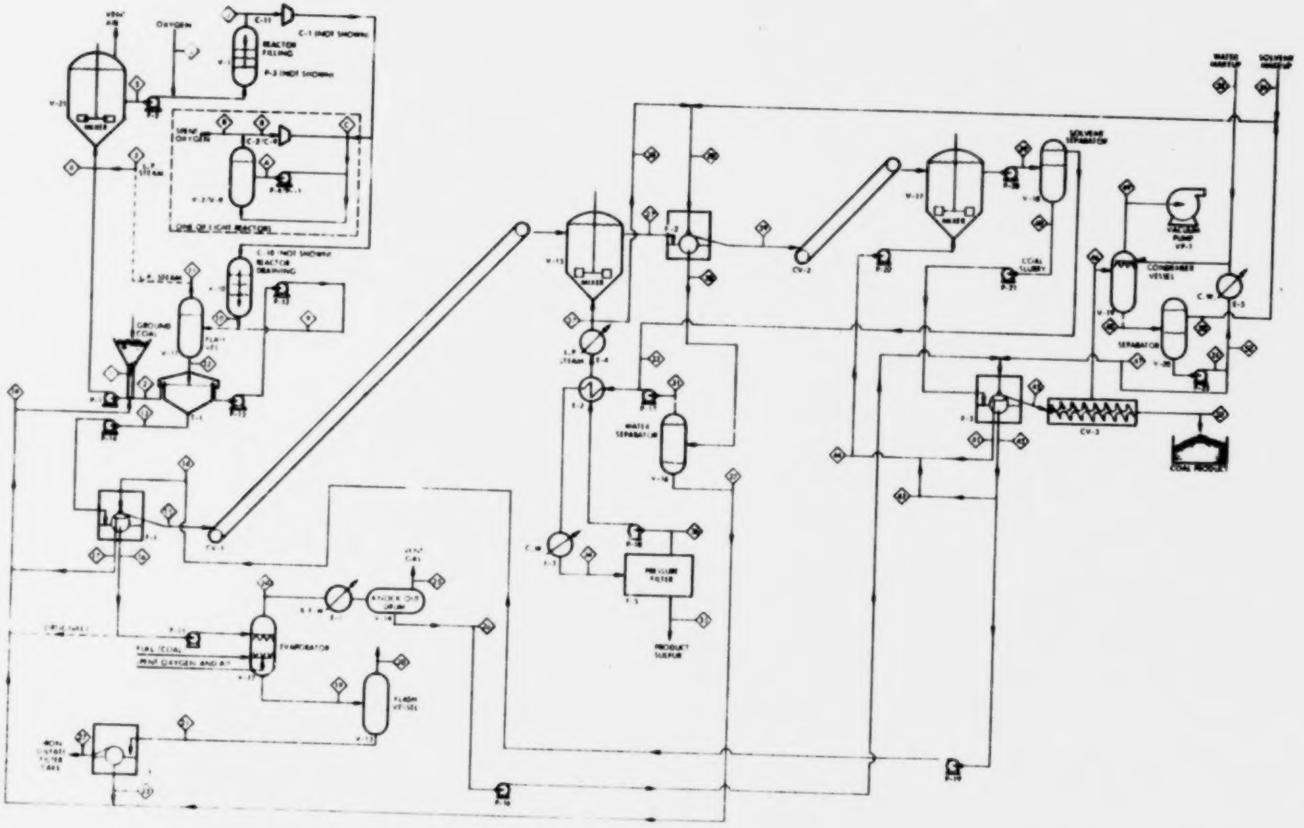

VENT AIR
OXYGEN
V-21
MIXER
C-11
C-1 (NOT SHOWN)
REACTOR FILLING
V-1
P-3 (NOT SHOWN)
VENT OXYGEN
C-2/C-9
V-2/V-9
ONE OF EIGHT REACTORS
L.P. STEAM
C-10 (NOT SHOWN)
REACTOR DRAINING
V-10
GROUND COAL
FLASH VESSEL
V-11
T-1
F-1
CV-1
VENT GAS
KNOCK OUT DRUM
V-14
E-1
EVAPORATOR
V-12
FUEL (COAL)
VENT OXYGEN AND AIR
FLASH VESSEL
V-13
IRON SULFATE FILTER CAKE
V-15
MIXER
L.P. STEAM
E-4
E-2
WATER SEPARATOR
V-16
C.W.
E-3
PRESSURE FILTER
F-3
PRODUCT SULFUR
F-2
CV-2
V-17
MIXER
P-20
COAL SLURRY
P-21
SOLVENT SEPARATOR
V-18
VACUUM PUMP
VP-1
CONDENSER VESSEL
V-19
C.W.
E-5
SEPARATOR
V-20
F-4
CV-3
COAL PRODUCT
WATER MAKEUP
SOLVENT MAKEUP

FIGURE 23. PYRITIC SULFUR REMOVAL PROCESS FLOW DIAGRAM

TABLE 29. PYRITIC SULFUR REMOVAL PROCESS MATERIAL BALANCE

	STREAM																			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Liquids, T/HR	10.0	229.8	1.3	400.0	400.5	-	-	-	250.0	407.5	-	656.2	177.0	50.0	33.4	143.6	50.0	158.9	80.3	-
Solids, T/HR	100.0	-		100.0	99.5	-	-	-	-	96.1	-	96.1	95.5	-	95.4	0.1	-	-	8.1	-
FLOWRATE, T/HR																				
Coal	94.0			94.0	94.0					94.0		94.0	94.0		93.9	0.1			0.1	
FeS_2	6.0			6.0	5.4					1.0		1.0	0.3		0.3					
S					0.1					1.1		1.1	1.2		1.2					
$FeSO_4$		8.6		10.9	18.6				9.3	5.9		15.2	6.5	0.1	0.8	5.4	0.5	2.3	5.4	
$Fe_2(SO_4)_3$		34.5		57.3	48.1				37.5	72.1		109.6	26.6	0.4	3.3	21.6	2.1	22.8	21.6	
H_2SO_4	0	2.0		3.5	5.9				2.2	0.7		2.9	1.5	0	0.2	1.2	0.1	1.5	1.2	
H_2O	10.0	184.7	1.3	328.3	327.9			0.06	201.0	328.8	1.3	528.5	142.3	49.5	29.1	115.4	47.3	132.3	60.1	nil
naphtha																				
O_2						3.84	3.48	0.19												
inert gas						0.02	0.02	0.02												
FLOWRATE, LB-MOL/HR																				
Coal (13.0)	14461.5			14461.5	14461.5					14461.5		14461.5	14461.5		14446.1	15.4			15.4	
FeS_2 (119.85)	100.0			100.0	90.0					17.0		17.0	5.0		5.0					
S (32.0)					8.0					66.4		66.4	76.0		76.0					
$FeSO_4$ (151.85)		113.1		143.2	245.2				123.0	77.8		200.8	87.1	1.2	11.0	70.7	6.6	30.1	70.7	
$1/2(Fe_2(SO_4)_3)$(199.85)		345.2		573.0	481.0				375.5	721.4		1096.9	265.8	3.7	33.4	215.6	20.5	227.8	215.6	
H_2SO_4 (98.0)	0.1	40.4		71.7	119.7				44.0	14.1		58.1	31.3	0.5	4.0	25.3	2.4	31.2	25.3	
H_2O (18.0)	1111.1	20521.7	143.0	35366.7	36429.8			6.6	22325.6	36528.8	143.0	58711.4	15806.5	5500.0	3233.3	12822.2	5251.0	14702.0	6672.7	nil
naphtha (93.2)																				
O_2 (32.0)						240.0	217.2	12.0												
inert gas (35.0)						1.2	1.2	1.2												

TABLE 29. CONTINUED

	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
Liquids, T/HR	80.3	-	80.3	-	-	55.3	235.5	50.2	23.6	262.1	233.4	28.7	14.2	246.4	-	246.4	200.9	45.5	119.8	105.6
Solids, T/HR	8.1	8.1	-	-	-	-	94.2	-	94.2	-	-	-	-	1.2	1.2	-	-	-	94.2	94.2
FLOWRATE, T/HR																				
Coal	0.1	0.1					93.9		93.9										93.9	93.9
Fe S_2							0.3		0.3										0.3	0.3
S							2.1	0.2	0.1	2.2	2.2		0.1	2.3	1.2	1.1	0.9	0.2	0.1	0
Fe SO_4	5.4	4.3	1.1				0.8		0.1	0.7		0.7							0.2	0.2
$Fe_2(SO_4)_3$	21.6	3.7	17.9				3.3		0.5	2.8		2.8							0.7	0.7
H_2SO_4	1.2	0	1.2				0.2		0	0.2		0.2							0	0
H_2O	50.1		60.1	58.5	3.2	55.3	29.1		4.1	25.0		25.0							100.0	100.0
naphtha							200.0	50.0	18.8	231.2	231.2		14.1	245		245.3	200.0	45.3	18.8	4.7
O_2				0.6	0.6															
inert gas				63.7	63.7															
FLOWRATE, LB-MOL/HR																				
Coal	15.4	15.4					14446.1		14446.1										14446.1	14446.1
Fe S_2							5.0		5.0										5.0	5.0
S							131.0	12.4	9.6	133.8	133.8		7.2	141.0	73.6	67.4	55.0	12.4	9.6	2.4
Fe SO_4	70.7	56.7	14.0				11.0		1.5	9.5		9.5							2.3	2.3
$1/2(Fe_2(SO_4)_3)$	215.6	37.0	178.6				33.4		4.7	28.7		28.7							7.2	7.2
H_2SO_4	15.3	0	25.4				4.0		0.6	3.4		3.4							0.9	0.9
H_2O	6672.7		6672.7	6505.0	355.5	6149.5	3233.3		455.0	2778.3		2778.3							11111.0	11111.0
naphtha							4291.8	1073.0	403.4	4961.4	4961.4		302.5	5263.9		5263.9	4291.8	972.1	403.4	100.9
O_2				40.0	40.0															
inert gas																				
CO_2				720.0	720.0															
N_2				3420.0	3420.0															

TABLE 29. CONTINUED

	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55
Liquids, T/HR	68.9	77.3	27.3	96.2	28.3	-	13.6	318.2	-	4.6	313.6	300.0	18.9	0.1	9.0
Solids, T/HR	-	-	-	-	94.2	-	-	-	-	-	-	-	94.2	-	
FLOWRATE, T/HR															
Coal					93.9								93.9		
Fe S_2					0.3								0.3		
S					0								0		
Fe SO_4	0	0.2	0.1	0.1	0								0		
$Fe_2(SO_4)_3$	0	0.6	0.2	0.2	0.1								0.1		
H_2SO_4	0	0	0	0	0								0		
H_2O	68.9	76.5	27.0	95.9	23.5	4.7	13.6	313.6	0.1		313.6	300.0	18.8		9.0
naphtha					4.7	4.7		4.6	0.1	4.6				0.1	
O_2															
inert gas															
FLOWRATE, LB-MOL/HR															
Coal					14446.1								14446.1		
Fe S_2					5.0								5.0		
S					2.4								2.4		
Fe SO_4	0.2	1.8	0.6	0.8	0.3								0.3		
$1/2(Fe_2(SO_4)_3)$	0.5	5.7	2.0	2.5	1.0								1.0		
H_2SO_4	0.1	0.7	0.2	0.3	0.1								0.1		
H_2O	7656.0	8500.0	3000.0	10656.0	2611.0	522.0	1506.0	34839.0	11.0		34839.0	33333.0	2089.0		995.0
naphtha					100.9	100.9		98.7	2.2	98.7				2.2	
O_2															
inert gas															

the feed stream to the reactor and the excess (1310 SCFM) is drawn from the reactor (7) and compressed (C-11) to about 70 psig for use in the other reactor vessels (V-2 to V-10).

Each of the reactor vessels is 100,000 gal capacity and requires one hour to fill. During this hour to fill, the reaction of pyrite and the regeneration of leach solution are occurring in the reactor. During the 15 minute residence time in the mixer the pyrite was about 10% reacted and the ferric/total iron ratio (Y) dropped from 0.80 to 0.66. During the fill time of the reactor, the reaction of pyrite reaches about 24% and the temperature increases to slightly over 220°F due to the heat of reaction and heat of regeneration.

When the vessel is full it is switched to a batch mode reactor as shown for vessels V-2 through V-9. The reactor is in this mode of operation for 8 hours until it begins the drain cycle. During batch mode operation, the slurry (A) is continuously aerated with oxygen (B) in an external loop. Pumps (P-4 through P-11) each circulate about 5000 gpm and the compressors(C-2 through C-9) each circulate about 100 SCFM of oxygen. When the oxygen content of the circulating gas (on a dry basis) falls below 90%, makeup oxygen (C) is added and some spent gas is vented (8). The 10% inert gas is principally argon and nitrogen which were present in the 99.5% oxygen feed and perhaps traces of nitrogen absorbed in the coal and not removed in the mixer (V-21). The continuous aeration maintains fine oxygen gas bubbles throughout the reactor volume and insures the reactor liquid will remain saturated with oxygen to provide the maximum rate of leach solution regeneration. In batch mode the reaction proceeds to 83% completion and, at the end of the 8 hour period, the temperature has increased to about 260°F. The vessels operate at a nominal 50 psig with an oxygen partial pressure of 30 psi. Since the vessels are about 60 feet in height, the pressure at the bottom of the vessel is about 35 psi higher than the gas pressure.

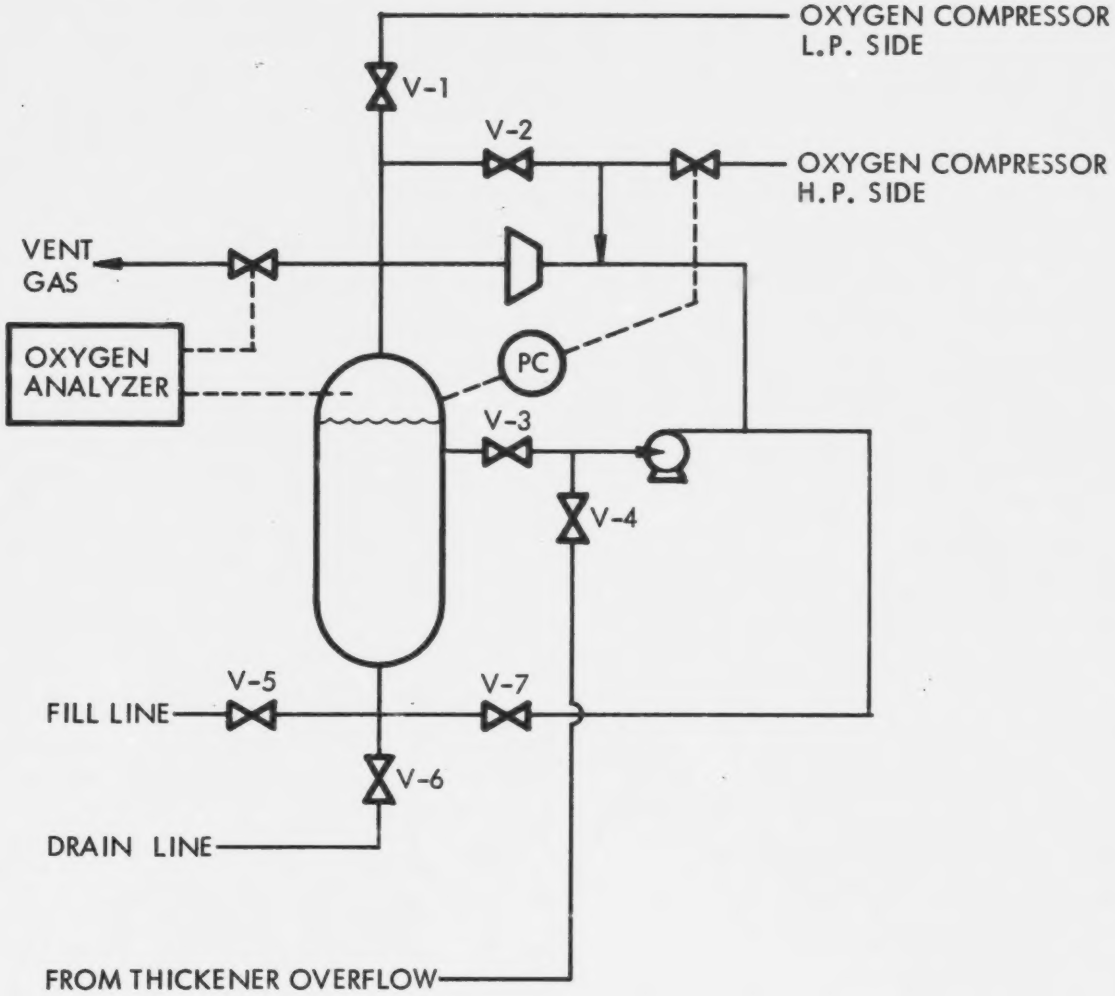
After 8 hours of reaction, the vessel begins the drain cycle. The contents of the reaction vessel (V-10) flow through the discharge line (10) to the flash vessel (V-11). At the same time, clear overflow leach solution from the thickener (T-1) is pumped through the slurry circulation loop (9) to clear it of slurry which could otherwise plug the lines or pump (P-12). This solution is blended with the draining slurry. The thickener solution is at a temperature of 205°F to 210°F so that the mixed stream temperature entering the flash vessel is controlled by the amount of leach solution added from the thickener. The oxygen pressure in the reactor vessel is maintained as the vessel drains to provide flow into the flash vessel which operates at 15 psig and 240°F. Fig.24 shows a reactor vessel with the piping and valving required for operation in each of the three modes: filling, reacting and draining.

The flash steam (11) from V-11 is used to provide solution reheat (3) and the quantity of low pressure steam is adjusted by the circulation rate in stream 9. The flash vessel is sized to hold the entire contents of one reactor in the event that it becomes necessary to discharge one reactor ahead of its normal drain cycle. In normal operation, the flash vessel feeds the thickener at substantially the same rate as liquid enters the flash vessel.

Feed to the thickener (12) is above the boiling point and some steam will flash upon entering the thickener. Most of the steam will condense on the thickener cover or the liquid surface. Excess steam could be vented from the thickener or from the flash vessel by decreasing its operating pressure.

The thickener is actually 2 units in parallel (each of which is 175 ft in diameter) and has 48,000 ft^2 of total surface area. At the thickener feed rate, the coal residence time in the thickener is about 3.6 hoursper foot of depth. The edge depth of 8 ft and the average depth of 11 ft give a total coal residence time between 30 and 40 hours. Only 24 hours of residence time is required to carry the pyrite removal from 83% in the thickener feed to 95% in the discharge slurry.

The underflow from the thickener (13) contains a nominal 35 wt% solids. The slurry is filtered by a rotary vacuum filter (F-1) with a separate circuit and accessories for washing the filter cake. About 960 ft^2 of filter area is required which is provided by two units each about 12 feet in diameter by 15 feet in length - one serving each of the thickeners. The filter cake wash (14) is provided by spent wash water and the wash filtrate (17) is recycled directly to the mixer feed circuit. The regular filtrate (16) is further processed, at least in part, to recover wash water and iron sulfate.


OXYGEN COMPRESSOR
L.P. SIDE
V-1
V-2
OXYGEN COMPRESSOR
H.P. SIDE
VENT
GAS
OXYGEN
ANALYZER
PC
V-3
V-4
V-5
V-7
FILL LINE
V-6
DRAIN LINE
FROM THICKENER OVERFLOW

VALVES OPEN DURING FILL: V-1, V-5
VALVES OPEN DURING REACTION: V-3, V-7
VALVES OPEN DURING DRAIN: V-2, V-4, V-6, V-7

FIGURE 24. REACTOR VALVING AND CONTROL

As shown in the process flow diagram, the filtrate (16) is pumped (P-15) to an evaporator vessel (V-12). This vessel could be a submerged combustor evaporator operating at elevated or atmospheric pressure. It seems more appropriate to operate with product coal as the fuel. The mass balance is based on processed coal (20% moisture) burned with air to give a flue gas, at 5% excess air, with a dew point of about 110°F. Assuming 85% thermal efficiency, the wash water evaporation requires 130 MM btu/hr. Vessel V-12 is a contactor which sprays the filtrate (16) into the combustion gases. The concentrated liquid and solids are withdrawn (19), the flash steam removed (20) if the liquid is superheated, and the slurry (21) is fed to a rotary filter (F-4). The 10% slurry would require 1600 ft^2 of surface area (two units 16 ft in diameter by 16 ft long). A more concentrated slurry can be obtained by processing less of the filtrate stream, but since the flow and handling characteristics of this slurry are not well-known, it seems prudent to select a more dilute slurry and accept the larger filter area estimate.

The combustion gas (24) is processed to recover evaporated water (26) for use in the washing section. The condenser (E-1) requires about 25,000 ft^2 surface are. The knockout drum (V-14) has a vent gas (25) flow rate of about 450 ft^3/sec and requires a diameter of about 24 ft to reduce the gas velocity to 1 ft/sec for droplet separation.

The filter cake (15) from filtration (F-1) of the thickener underflow is conveyed (CV-1) to a mixing vessel (V-15). The coal, wet with leach solution, is slurried with 1250 gpm of a light naphtha (37) in the C_6-C_7 boiling range. A mixer volume of 40,000 gallons gives 0.5 hour residence time for the sulfur to be dissolved into the naphtha solvent. At 160°F naphtha will dissolve 1.4% by weight sulfur. The solvent/coal ratio results in a 1.0% mixer effluent (27). The slurry is filtered (F-2) using a rotary vacuum filter with about 500 ft^2 of surface. The cake as first formed on the filter cloth is wet with high sulfur naphtha containing 1.0% sulfur (Stream 27 has 2.1 tons per hour of sulfur and 200 tons per hour of solvent). Prior to discharge from the filter, the cake is washed with low sulfur solvent (Stream 28 is 0.4% sulfur) which dilutes and displaces a part of the high sulfur naphtha. The residual naphtha on the cake (29) is estimated to contain about 0.8% sulfur. The cake (29) is expected to have 20%

naphtha and 5% aqueous leach solution (dry coal basis). The combined wash and filtrate (30) is settled and separated in a 25,000 gallon vessel (V-16). The aqueous leach solution (32) is returned to the leach solution circuit while the sulfur-rich solvent is cooled (E-2) from 160°F to 110°F by exchange with the returning naphtha (36). The exchanger area is about 12,000 ft^2 to exchange about 14 MM btu/hr. The naphtha is further cooled from 110°F to 90°F to precipitate additional sulfur. The cooling requires about 3,300 ft^2 of exchanger area (E-3) to reject 6 MM btu/hr to cooling water. The cooled naphtha is pressure filtered (F-5) in a 6 ft square, 50 plate press with about 1800 ft^2 of filter area. Product sulfur (35) is recovered at the rate of 1.2 T/hr (25 LT/D). The sulfur-lean filtrate (36) which contains 0.44% sulfur, is reheated to 140°F by exchange (E-2) with the hot naphtha and then steam heated (E-4) from 140°F to 160°F. The steam heater requires 6 MM btu/hr of heat and has 700 ft^2 of surface area.

The filter cake (29) from the solvent filter (F-2) is conveyed (CV-2) to the wash water mixer (V-17). The naphtha wet coal is mixed with a low salt wash water (44) in a 50,000 gal mixer to give 1 hour of residence time. The effluent stream (39) is pumped to a 25,000 gal settling tank (V-18) where the naphtha is skimmed and returned (33) to the naphtha circuit. The coal and wash water slurry (40) is filtered in rotary vacuum filters (F-3) which are the same as the leach filters (F-1). Cake washing is with condensate water (26) from the knockout drum (V-14) and water (47) from the final drying. The wash water filtrate (41) and a portion of the regular filtrate (43) are combined (44) and fed to the wash water mixer (V-17).The remainder of the regular filtrate (14) is pumped to the thickener underflow filter for washing the cake.

The filter cake (45) which contains 25% wash water and 5% naphtha (dry basis) is fed to a variable pitch screw conveyor (CV-3). The close pitch at both ends compacts the coal to produce low gas leakage.

The center portion of the conveyor is evacuated to vaporize the naphtha and part of the wash water. The sensible heat of the wet coal will provide the heat of vaporization for the naphtha and for about 5% of the water. A small quantity of heat may be required to maintain the coal at 130°F in the vaporization section. The vapors (46) are condensed in a water sprayed vessel (V-19) fed with 1250 gpm of water at 90°F. The effluent (48) is sent to a 25,000 gal separation vessel (V-20) at 110°F. The naphtha (50) and make up naphtha (54) are returned to the naphtha circuit. The water from the separator (51) is divided with a portion (47) going to the wash filter and the balance (52) passing through a 1.500 ft^2 cooler (E-5) where 12 MM btu/hr are removed to decrease the temperature to 90°F. This cooled water and the make up water (55) are combined to provide the cool water spray for the condenser.

The coal product (53) is 94.2% (dry basis) of the coal fed. Approximately 5% of this product is used to provide for the heat requirements which gives a net weight yield of about 90%. The product contains 20% moisture and the following maximum sulfur content based on 3.2% pyritic sulfur in the feed (based on dry coal weight):

Organic sulfur - no change
Pyritic sulfur - 0.17%
Elemental sulfur - 0.04%
Added sulfate sulfur - 0.03%
0.24% + organic sulfur

Experimentally it has been determined that the ash decreases about 30%(from 20% ash to 14% ash) and the heat of combustion increases about 5% (from 12,300 btu/lb to 12,900 btu/lb). These are in excellent agreement with the change that is expected when pyrite equivalent to 3.2% sulfur is removed from the coal.

3.2.5 Process Cost Estimation

Throughout the bench-scale development project, process costs have frequently been reviewed with an objective of focusing experimental effort in the areas of greatest cost sensitivity. The capital cost of equipment required to perform the pyrite leaching must be carfully controlled to maintain a low processing cost per ton of coal product. As will be seen in the capital estimate presented in the following discussion, the major capital cost continues to be in the reactor section. Following closely are capital requirements in the separation section and in the sulfate removal section (which also recovers the wash water).

As the process development progressed and additional experimental data were obtained, some complications were identified and some process simplifications were demonstrated. The net result is that at the conclusion of this bench-scale effort, the process for removing pyritic sulfur from coal remains highly attractive and sufficient data has been obtained to provide confidence in the economic viability of the process.

Baseline Process Cost Estimate

The previous section of this report presented a conceptual process design and process flow sheet for removing 95% of the pyritic sulfur from a coal which initially contained 3.2% pyritic sulfur. The major equipment for the process is given in Table 30 and identified with the equipment on the flow sheet (Fig.23). The equipment was selected and sized to approach the optimum cost for processing this high pyrite coal to the 95% removal level. Costs were obtained primarily from published data at 1968 prices and were updated to current cost by adding the 21% increase indicated by the Chemical Engineering Plant Construction Index for the period 1968 to November 1972.

The total estimated processing cost has been determined as follows:

TABLE 30. PYRITIC SULFUR REMOVAL PROCESS MAJOR EQUIPMENT LIST

FEED AND MIXING SECTION - \$0.08MM

1.		Ground Coal Hopper - 5000 ft^3
2.		Screw Feeder - 16"Ø x 20', 5 HP motor
3.	P-1	Feed Pump - 1650 gpm, 15 psi, 25 HP motor, stainless steel (SS)
4.	V-21	Mixing Vessel - 25,000 gal, atmospheric, SS
5.		Agitator - 25 HP, SS
6.	P-2	Discharge Pump - 1650 gpm, 60 psi, 75 HP motor, SS

REACTOR SECTION - \$2.81MM

1.	C-11	Oxygen Compressor - 1310 SCFM, C.R.=1.7, 90 HP motor
2.	C-1/10	Recycle Compressors (10) - 100 SCFM, C.R.=1.6, 7.5 HP motor
3.	P-3/12	Circulation Pumps (10) - 5000 gpm, 15 psi, 75 HP motor, SS
4.	V-1/10	Reaction Vessels (10) - 100,000 gal, 50 psig, SS clad

SEPARATION SECTION - \$2.07MM

1.	V-11	Flash Drum - 100,000 gal, 15 psig, SS clad
2.	T-1	Thickeners (2) - 175'Ø x 8' wall, 2MM gal, covered, SS
3.	P-13	Overflow pumps (2) - 850 gpm, 15 psi, 7.5 HP motor, SS
4.	P-14	Underflow pumps (2) - 900 gpm, 10 psi, 7.5 HP motor, SS
5.	F-1	Rotary Vacuum Filters (2) - 480 ft^2, wash circuit

SULFATE REMOVAL SECTION - \$1.27MM

1.	P-15	Evaporator Feed Pump - 500 gpm, 15 psi, 10 HP motor, SS
2.	V-12	Evaporator Vessel - 25'Ø x 55', spray nozzles, 5 psig, SS
3.		Furnace Firebox - 130 MM btu/hr, coal fired
4.	E-1	Wash Water Condenser - 25,000 ft^2, SS tubes
5.	V-14	Knockout Drum - 24'Ø x 30', atmospheric
6.	P-16	Condensate Pump - 250 gpm, 20 psi, 3 HP motor
7.	V-13	Flash Vessel - 25,000 gal, 15 psig, SS
8.	F-4	Rotary Vacuum Filters (2) - 800 ft^2

TABLE 30, CONTINUED

SOLVENT EXTRACTION SECTION - $0.59MM

1.	V-15	Mixing Vessel - 40,000 gal, atmospheric, SS
2.		Agitator - 100 HP, SS
3.	CV-1	Feed Conveyor - screw 24"Ø x 150', 50' lift, 25 HP motor, SS
4.	F-2	Rotary Vacuum Filter - 500 ft^2, wash spray
5.	V-16	Separator Tank - 25,000 gal, atmospheric, SS
6.	E-2	Heat Exchanger - 12,000 ft^2
7.	E-3	Solvent Cooler - 3,300 ft^2
8.	E-4	Solvent Heater - 700 ft^2
9.	P-17	Filter Feed Pump - 1600 gpm, 20 psi, 25 HP motor SS
10.	P-18	Mixer Feed Pump - 1600 gpm, 15 psi,25 HP motor, SS
11.	F-5	Plate Filter - 1,800 ft^2
12.		Sulfur Melter - .15MM btu/hr, 260°F
13.		Solvent Stripper and Vapor Recovery - 20 SCFM
14.		Liquid Sulfur Storage Pit - 15,000 gal, 260-280°F, covered

WATER WASH SECTION - $0.64MM

1.	V-17	Mixing Vessel - 50,000 gal, atmospheric, SS
2.		Agitator - 100 HP, SS
3.	CV-2	Feed Conveyor - screw 24"Ø x 150', 50' lift, 25 HP motor, SS
4.	P-22	Mixer Feed Pumps - 400 gpm, 15 psi, 5 HP motor, SS
5.	P-20	Mixer Drain Pump - 800 gpm, 15 psi, 7.5 HP motor, SS
6.	V-18	Separator Tank - 25,000 gal, atmospheric, SS
7.	F-3	Rotary Vacuum Filters (2) - 480 ft^2, wash circuit
8.	P-21	Filter Feed Pump - 750 gpm, 10 psi, 5 HP motor, SS
9.	P-19	Filtrate Pump - 200 gpm, 20 psi, 3 HP motor, SS
10.	CV-3	Screw Conveyor - 20"Ø x 350' long, vacuum, variable pitch, 100 HP motor, SS
11.	VP-1	Vacuum Pump - 400 lbs/hr, 80 SCFM, 2 psia
12.	V-19	Condenser Vessel - 20,000 gal, 10'Ø x 30', vacuum. water spray
13.	V-20	Separation Tank - 25,000 gal, atmospheric
14.	E-5	Heat Exchanger - 1,500 ft^2
15.	P-23	Condensate Pump - 1,200 gpm, 20 psi, 25 HP motor, SS
16.		Makeup Water Pump - 50 gpm
17.		Makeup Solvent Pump - less than 1 gpm

TOTAL ESTIMATED CAPITAL - $7.46MM

Capital Related Costs:	Annual Cost,1000$
Depreciation - 10% straight line	746
Maintenance, insurance, taxes, interest	746
Labor:	
Labor, 3.3 operating positions	330
Utilities:	
Electrical power - 1000 KW (5mil/Kw-hr)	40
Cooling water - 20°F rise; 2000 gpm (2¢/1000 gal)	10
Heating-130 MM btu/hr; coal, 5T/hr	-
Boiler feed water	nil
Materials:	
Oxygen 99.5%, 3.8T/hr ($10/T)	304
Solvent, 200 lb/hr (3¢/lb)	48
TOTAL COST	2224

Feed coal 100T/hr, 0.8MMT/yr	$ 2.78/T
Coal yield (weight basis)	90%
Coal yield (btu basis)	95%

The added cost of energy may also be considered for the base line coal. If the baseline coal is similar to the Lower Kittanning coal utilized in our laboratory studies, it will contain 20% ash and have a heating value of 12,300 btu/lb as fed. After processing the coal will be 90% recovered, have 14% ash, and have a heating value of 12,900 btu/lb. With feed coal priced at $6.00/T the feed costs 24¢/MMbtu. After processing the available energy costs 38¢/MMbtu.

Applicability to Other Coals

The baseline case was selected to be a plant processing coal similar to the sample of Lower Kittanning coal used in bench-scale testing. This is an unusually high ash, high pyrite coal. Consideration was given to a sample of Lower Kittanning coal from the Cush Creek mine (also of Indiana County, Pennsylvania) with 0.8% pyritic sulfur and 13,600 btu/lb. To meet standards of performance for new stationary source combustion operations, which limit allowable sulfur oxide emissions to 1.2 lbs/10^6btu of heat input, only 71% of the starting pyrite must be removed. To process this coal in an optimum manner a process redesign would be required, but the following approximation to the correct capital cost was made based on 100T/hr of coal feed.

Feed and Mixing Section: unchanged - $0.08MM.

Reactor Section: 4 rather than 10 reactors with a 3:1 leach solution to coal ratio. Each reactor 80,000 gal, 25 HP oxygen compressor, 4000 gpm circulating pumps - $1.20MM.

Separation Section: 80,000 gal flash drum, no thickeners, the 25% slurry is filtered directly, 4 filters required - $0.72MM.

Sulfate Removal Section: only 1 filter of 250 ft^2 required. Remainder about unchanged - $1.05MM.

Solvent Extraction Section: heat exchanger duties reduced about 75% and the sulfur filter area required reduced to about 450 ft^2 - $0.46MM.

Water Wash Section: unchanged - $0.64MM.

Total Capital Cost Estimate: $4.15MM.

The estimated processing cost is as follows:

			Annual Cost, 1000 $
Capital Related Costs - 10% straight line			415
Maintenance, insurance, taxes, interest			415
Labor:			
Labor - 3 operating positions			300
Utilities:			
Electrical power - 750 KW			30
Cooling Water - 2000 gpm			10
Materials:			
Oxygen, 1.0T/hr ($12/T)			96
Solvent - 200 lb/hr			48
			1314
Feed Coal 100T/hr, 0.8MM T/yr		$ 1.64	
Coal Yield (weight basis)	94%		
Coal Yield (btu basis)	95%		

It is evident that coals of the Lower Kittanning type will generally range from $2.00 per ton if the pyritic sulfur content is about 1% to about $3.00 per ton if the pyritic sulfur content is about 3.5%. Another type of coal examined during the bench-scale program was Illinois

No.6. This coal contains about 2% pyritic sulfur but because of the high organic sulfur content it would not meet the new source performence standards even with total pyritic sulfur removal. If it were to be processed to remove 95% of the pyrite, the baseline process and cost estimate would show little change. The Illinois coal contains about one-half the pyrite of the baseline Lower Kittanning coal, but has side reactions which consume ferric ion. The oxygen and solution volumes would be about the same as with the baseline process. There would be some reduction in the reactor residence time, the number of filters and the extraction solvent circulation rates. However, the filter cakes have higher liquid levels and a second stage of washing would probably be required. It is expected that the cost increases and decreases would about balance and both capital and operating cost would be similar to the baseline case.

Based on the current conceptual process design, it is concluded that a broad spectrum of Eastern coals can be processed at costs in the range of $2.00 to $3.00 per ton. It was assumed in developing these costs that the pyrite removal plant is coordinated with a power plant which will have the principal off-site facilities such as coal grinding facilities, change house, offices, rail facilities, etc. To the extent that these off-sites are not available or for bookkeeping purposes are prorated to the coal processing cost, the direct costs given above will be increased. These additional charges, if any, will clearly be related to the specific situation and can not be reasonably generalized.

3.3 Organic Sulfur Removal

The process concept, correlation of laboratory results, bench-scale results, process design studies and process cost estimations for an organic sulfur removal technique are presented in the sections to follow.

3.3.1 Process Concept.

Utilizing the Meyers' Process for removal of pyritic sulfur alone would allow conversion of a major portion of the coal production in the United States east of the Mississippi River from a sulfur content of 2 to 4% to a sulfur content of 0.5 to 1.0% after the process is fully optimized. This would allow a significant reduction in sulfur oxide pollution from combustion of coal. However, eventually it will be desirable to remove additional sulfur from coal prior to combustion in order to minimize sulfur oxide pollution. This means the removal of sulfur from coal which is bonded into the organic coal matrix. An approach for the removal of this type of sulfur was investigated in this program and is described below.

This approach attemps to extract organic sulfur (which is thought to be in aromatic polymers of varying molecular weight) through a solvent partitioning of the organic coal matrix between an undissolved and dissolved portion. In this approach, pulverized coal is extracted with solvents which tend to depolymerize and dissolve that part of the organic matrix richer in organic sulfur.

A block diagram showing the processing steps currently envisioned for the removal of organic sulfur from coal is presented in Figure 25. In this process, pulverized coal is contacted with a leaching solvent which separates the organic sulfur compounds from the coal matrix and dissolves them into the solvent. The bulk of the leach solution exiting the organic sulfur leacher with the coal is separated from the coal and recycled to the leacher. Any residual leach solvent remaining with the coal is evaporated from the coal and carried by an inert gas to a condenser where it is condensed, separated from the inert gas and recycled to the leaching unit. The dry processed coal is then conveyed to storage.

The overflow solution exiting the organic sulfur leacher is pumped to the leach solvent vaporizer where the bulk of the leach solution is evaporated and then condensed and recycled to the organic sulfur leacher. The high sulfur residue slurry exiting the leach solvent vaporizer is further dried by the contacting of the slurry with a hot gas in a drying chamber (e.g., spray drier). The hot gas is cooled and the leach solvent is condensed and separated for recycle to the organic sulfur leacher. Vacuum flash distillation is an alternate for spray drying. After solvent removal, the dried high sulfur solid residue is conveyed to storage.

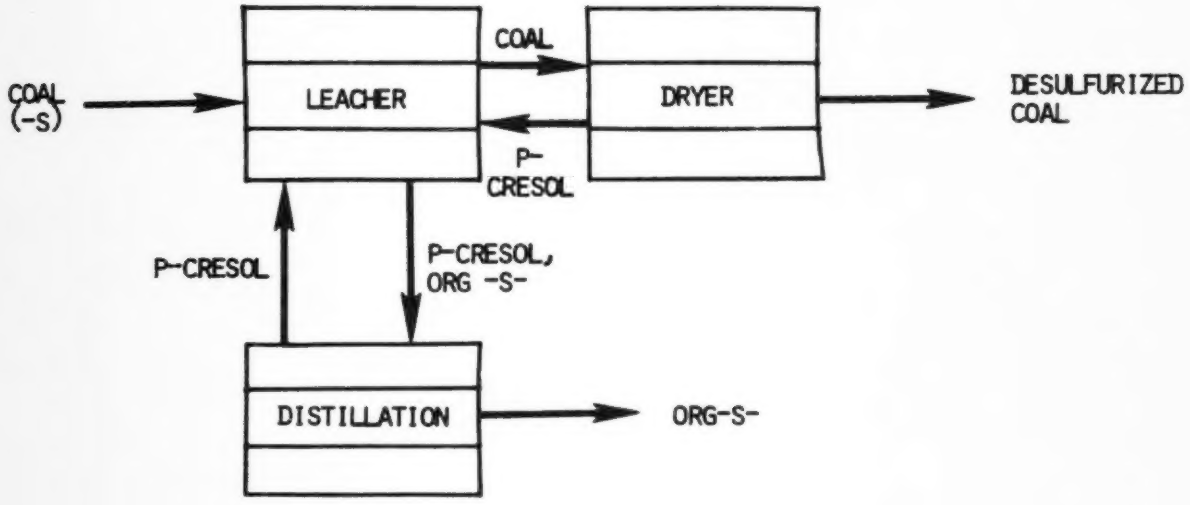

COAL
(-S)
LEACHER
COAL
DRYER
DESULFURIZED
COAL
P-
CRESOL
P-CRESOL
P-CRESOL,
ORG -S-
DISTILLATION
ORG-S-

Figure 25. Organic Sulfur Removal Process Block Diagram

3.3.2 Correlation of Laboratory Results

A screening study was performed on coals from four coal beds in a previous program, and it was found that p-cresol was the most promising solvent for reduction of the organic sulfur content of coal.

Some typical results for organic sulfur removal based on sulfur analyses before and after extraction are shown in Table 31 for No.V (5) bed coal.

Table 31. Removal of Organic Sulfur from No.V (5) Seam Coal via P-Cresol Extraction

Coal	% Organic Sulfur Before Extraction	% Organic Sulfur After Extraction
Indiana No.V	1.75	1.00
Illinois No.5	1.96	1.15
	% Total Sulfur Before Extraction	% Total Sulfur After Extraction
Indiana No.V	3.48	2.76,2.78,2.80
Illinois No.5	3.59	2.77

Removal of 30-40% or organic sulfur is implied by both total sulfur and sulfur forms analyses. The results for Indiana No.V were obtained as a part of a screening study during the previous program (11), while data for Illinois No.5 was obtained as a part of the present program. The two beds correlate; i.e., they are actually the same seam and, for all practical purposes, give the same results when extracted with p-cresol.

Bench-scale studies for removal of organic sulfur were performed on Lower Kittanning and Illinois No.5 coals as part of the program reported here. These studies indicated that 30-50% of the organic sulfur content of the above two coals is removed by p-cresol treatment at 200°C; however, the sulfur removal could not be confirmed by analysis of the extracts. The previous studies (11) were based only on analyses of the coal samples. Results are shown in Table 32 for extraction of the Illinois No.5 coal with p-cresol.

Table 32. Organic Sulfur Removal from Illinois No.5 Coal

	Organic Sulfur Removal, %		
Mesh	Recovered S	ΔS_t Coal	S Forms
-14	11	32	30
-100	9	34	26

These results show that organic sulfur removal calculated on the basis of differential sulfur values on starting and treated coals or on differential organic sulfur content of starting and treated coals indicated approximately 30% removal, while calculations based on sulfur analyzed in the extract fractions shows only 9-11% removal. These and other similar extractions are described in detail in the following section.

3.3.3 Bench-Scale Experimentation

The laboratory screening results on organic sulfur removal from coal, described above, indicated sufficient promise to justify a more detailed investigation of the process in bench-scale. The objectives of the bench-scale study on organic sulfur removal from coal were: verification of laboratory results through careful process and sulfur mass balance, process definition through unit operation parametric investigations, and generation of necessary information for pilot and commercial plant preliminary designs.

3.3.3.1 Experimental Apparatus and Procedures

Two coals were selected,with Environmental Protection Agency approval, for bench-scale investigation : Illinois No.5 and Lower Kittanning. Criteria for selection, starting coal analyses, and sampling procedures were presented in detail in the pyritic sulfur removal section (Sections 3.1 and 3.2.3.1). These coals were extracted with each of two solvents: p-cresol and nitrobenzene. Effects of extraction temperature and time, coal particle size, and coal moisture on process efficiency were investigated. Solvent retention on processed coal and extent of coal dissolution were also determined. A substantial effort was expended for complete recovery of removed organic sulfur.

Figure 26 is a block diagram of the bench-scale apparatus used in this investigation. It consists of four unit operations involving extraction (coal leaching with the solvent), filtration (coal separation from the majority of spent solvent), drying (complete solvent separation from coal), and solvent regeneration (separation of solvent from dissolved organic sulfur and coal residue by distillation). The apparatus was designed to minimize transfer and evaporation losses so that meaningful process and sulfur mass balances were attainable. As Figure 26 indicates sample trapping and analysis were frequent throughout the process. The majority of solid sample analyses were performed at CT&E (Commercial Testing and Engineering Co.); liquid fractions were analyzed at TRW.

Coal samples varied in size from approximately 100 to 500 grams depending on the parameters investigated. The smaller size samples were used, when possible, because they permitted more expeditious control of processing losses. The majority of extractions were performed at the reflux temperature of the slurry (coal-solvent mixture); when dry coal samples were used, this temperature very nearly corresponded to the normal boiling point of the solvent. In the baseline case, the coal sample and hot solvent were mixed in the leacher, brought quickly to boiling and allowed to reflux for one hour. At the end of the hour the hot slurry was vacuum filtered in a closed, well-trapped filtration unit. The coal, "wet" with spent solvent, was rinsed with fresh solvent and transferred to a trapped vacuum oven where it was dried overnight at approximately 150°C. The liquids driven off the coal (principally solvent and, in cases of high moisture content coals, some water) were collected and analyzed for sulfur. The spent solvent (filtrate) was sampled and transferred to a heated vacuum distillation flask where it was slowly distilled to near dryness. The distillate (normally pure solvent) was analyzed and, if pure, reused. The tar-like residue was vacuum dried further to complete dryness, weighed, and analyzed for total sulfur and occasionally sulfur forms, ash, and heat content. The processed coal was analyzed for moisture, total sulfur (Eschka and an occasional "bomb wash" as a check), ash, heat content, sulfur forms, and nitrogen. The nitrogen analysis served as a direct indication of solvent retention in the case of nitrobenzene extractions and as an indirect indication (dilution effect) in the p-cresol extractions. The liquid fractions were analyzed for total sulfur by x-ray fluorescence; a number of "bomb wash" and "lamp combustion" analyses were also performed as checks.

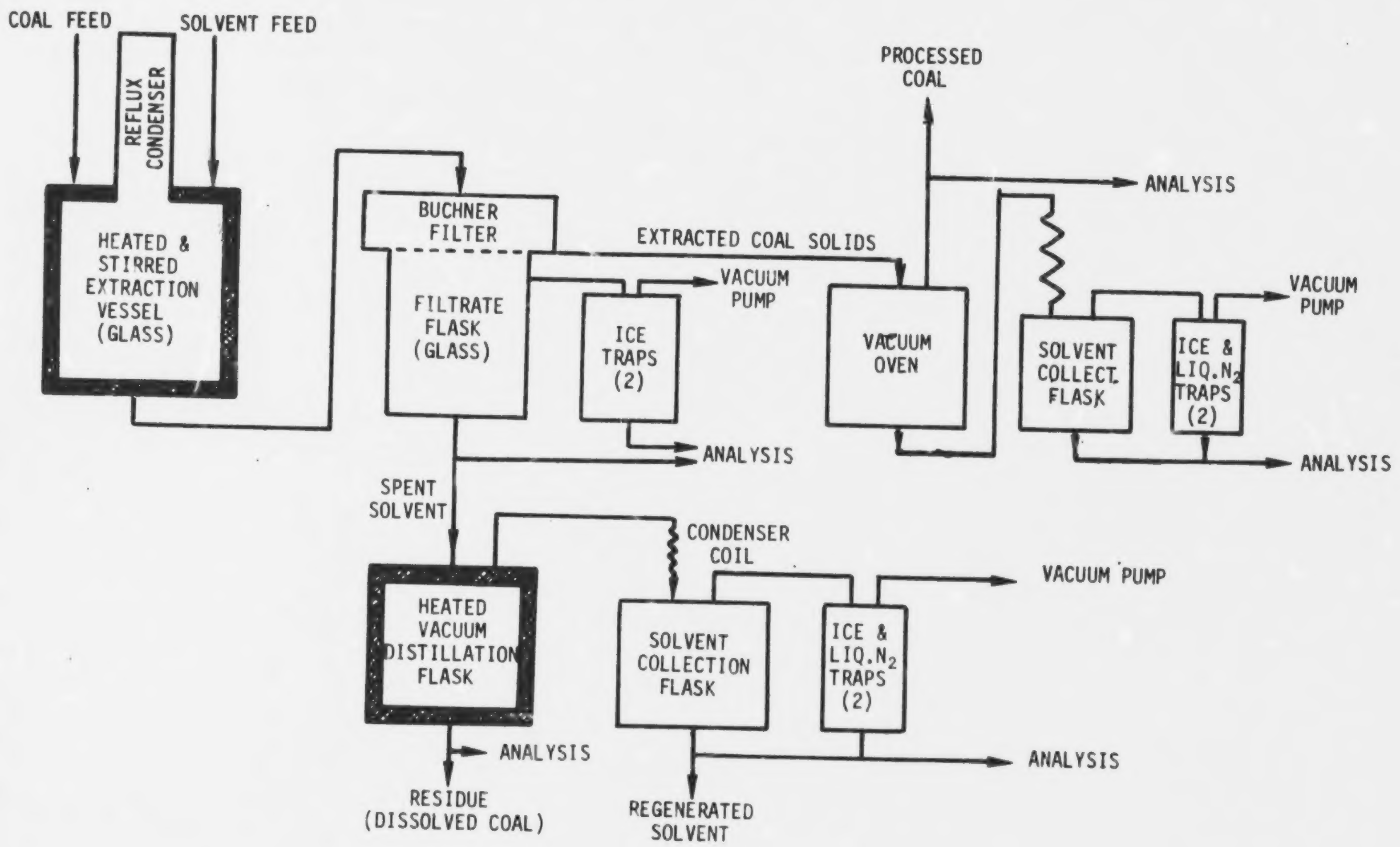

COAL FEED
REFLUX CONDENSER
SOLVENT FEED
HEATED & STIRRED EXTRACTION VESSEL (GLASS)
BUCHNER FILTER
FILTRATE FLASK (GLASS)
ICE TRAPS (2)
VACUUM PUMP
ANALYSIS
EXTRACTED COAL SOLIDS
VACUUM OVEN
PROCESSED COAL
ANALYSIS
SOLVENT COLLECT. FLASK
ICE & LIQ.N$_2$ TRAPS (2)
VACUUM PUMP
ANALYSIS
SPENT SOLVENT
HEATED VACUUM DISTILLATION FLASK
ANALYSIS
RESIDUE (DISSOLVED COAL)
CONDENSER COIL
SOLVENT COLLECTION FLASK
ICE & LIQ.N$_2$ TRAPS (2)
VACUUM PUMP
ANALYSIS
REGENERATED SOLVENT

FIGURE 26. BENCH-SCALE ORGANIC SULFUR REMOVAL APPARATUS

3.3.3.2 Results and Discussion

The bulk of organic sulfur extraction data from Illinois No.5 and Lower Kittanning coals is presented in three tables in this section. These tables show the experimental conditions, the process and sulfur mass balances, and the final coal composition (extracted coal). The data represent the results of 48 experiments (some of them duplicates) performed during the study of process parametric effects on organic sulfur removal from "as received" and dried coals.

Tables 33 and 34 are identical in information presented and format. They summarize the data obtained from a 36 experiment matrix designed to investigate the effects of solvent, coal particle size and extraction time on organic sulfur removal from "as received" Illinois No.5 (Table 33) and Lower Kittanning (Table 34) coals. The extractions were performed at slurry reflux temperatures with both coals. The observed small fluctuations in extraction temperature within each coal and the large difference in this extraction parameter between coals are due to the variance in moisture content of the samples. It is believed that the solvent displaced the water from the coal and the "dissolved" water lowered the reflux temperature of the mixture in proportion to each concentration. Thus, the Illinois No.5 coal samples with 10 to 12 wt% water refluxed at 120°C ±6°C, while the Lower Kittanning coal samples with approximately 1% water refluxed at 185°C ±10°C.

Each table is separated in two parts. Part 1 contains important experimental parameter information, the process mass balance, and the estimated solvent retention on each treated (processed) coal sample. Note that 100 mesh top size coals were processed in duplicate. The "coal sample in" (7th column) weight is balanced against the "total coal out" weight (11th column) which includes the weights of the treated coal (recovered after filtration and drying of the extraction slurry) and the "dissolved coal" present in the filtrate. The latter consists of dissolved solids (organic matrix) and extracted moisture (water). The weight of the "solids" (dissolved coal and sulfur) was obtained by distillation of the filtrate to dryness and subsequent vacuum drying of the residue. The water "dissolved" (removed by solvent from the coal sample during processing) was computed

TABLE 33. ORGANIC SULFUR EXTRACTION FROM ILLINOIS NO.5 COAL ("AS RECEIVED" COAL)

Part 1. Experimental Conditions and Process Mass Balance

Experiment Number	EXPERIMENTAL CONDITIONS					PROCESS MASS BALANCE, GRAMS													
	Solvent	Coal Mesh	Extraction		Filtration Time (Minutes)	Coal Sample In(a)	Dissolved Coal		Treated Coal Dried	Total Coal Out(d)	Solvent Retained(e)	Solvent Recovered		Solvent Transfer Losses	Total Solvent Out(g)	Solvent In		Water from Coal	Total Solvent In(g)
			Time (Minutes)	Temp. (°C)			Solids(b)	Water(c)				Filtrate Distillate	Drier Traps(f)			Extraction	Rinse		
0-1	p-Cresol	-14	30	123	10	93.4	5.5	9.4	83.6	98.5	5.1	332.6	78.9	20.4	437.0	338.9	88.7	9.4	437.0
0-2	p-Cresol	-100	30	124	10	97.8	5.8	9.9	93.0	108.7	10.9	299.0	118.6	22.0	450.5	361.6	79.0	9.9	450.5
0-3	p-Cresol	-100	30	125	10	95.0	5.4	9.6	93.7	108.7	13.7	270.6	112.7	19.1	416.1	360.5	46.0	9.6	416.1
0-4	Nitrobenzene	-14	30	122	15	92.0	5.9	9.3	81.4	96.6	4.6	340.8	78.6	17.5	441.5	377.3	54.9	9.3	441.5
0-5	Nitrobenzene	-100	30	113	10	96.9	6.0	9.8	90.5	106.3	9.4	264.2	126.3	19.7	419.6	361.6	48.2	9.8	419.6
0-6	Nitrobenzene	-100	30	115	10	86.1	5.7	8.7	79.1	93.5	7.4	298.4	106.8	19.7	432.3	364.9	58.7	8.7	432.3
0-7	p-Cresol	-14	60	126	10	97.3	8.6	9.8	86.9	105.3	8.0	300.6	122.3	29.2	460.1	387.4	62.9	9.8	460.1
0-8	p-Cresol	-100	60	131	10	93.6	7.7	9.5	85.3	102.5	8.9	401.7	79.3	25.8	515.7	384.6	121.6	9.5	515.7
0-9	p-Cresol	-100	60	124	10	93.4	9.2	9.4	83.8	102.4	9.0	291.7	119.2	27.3	447.2	374.2	63.6	9.4	447.2
0-10	Nitrobenzene	-14	60	136	15	90.8	4.3	9.2	78.3	91.8	1.0	329.7	88.3	25.4	444.4	376.7	58.5	9.2	444.4
0-11	Nitrobenzene	-100	60	132	15	92.0	7.1	9.3	81.5	97.9	5.9	305.9	118.8	16.4	447.0	397.2	40.5	9.3	447.0
0-12	Nitrobenzene	-100	60	122	10	91.5	6.8	9.2	81.6	97.6	6.1	292.6	126.2	34.7	459.6	370.6	79.8	9.2	459.6
0-13	p-Cresol	-14	120	121	15	93.5	7.1	9.5	84.1	100.7	7.2	334.2	73.8	22.7	437.9	338.2	90.2	9.5	437.9
0-14	p-Cresol	-100	120	123	10	90.2	7.3	9.1	80.2	96.6	6.4	308.2	108.5	25.4	448.5	357.2	82.2	9.1	448.5
0-15	p-Cresol	-100	120	123	10	90.4	7.8	9.1	83.6	100.5	10.1	289.8	109.7	20.4	430.0	356.4	64.5	9.1	430.0
0-16	Nitrobenzene	-14	120	114	10	90.0	4.5	9.1	80.0	93.6	3.6	350.7	91.9	13.2	459.4	401.2	49.1	9.1	459.4
0-17	Nitrobenzene	-100	120	119	20	92.7	4.9	9.4	85.4	99.7	7.0	279.9	116.1	21.1	424.1	358.8	55.9	9.4	424.1
0-18	Nitrobenzene	-100	120	114	12	90.0	5.4	9.1	83.3	97.8	7.8	270.6	109.8	20.7	408.9	360.9	38.9	9.1	408.9

(a) As used (high moisture content). (b) Residue recovered from distillation of extraction slurry filtrate. (c) Estimated from water loss of "as used" coal sample dried under conditions identical to the extracted coal conditions (150 C under vacuum). (d) Includes dissolved coal (residue + water). (e) Estimated. This value is subject to the errors in the "dissolved water" weight and it would be high by the amount of solids lost during operational transfers (0.5 gram to 1.0 gram normally. (f) Obtained by difference from wet coal (after filtration) and dried coal sample weights. (g) Includes water from coal.

TABLE 33. CONTINUED

Part 2. Analytical Data and Sulfur Mass Balance

Exp. No.	Sample Total Sulfur (wt%)	TOTAL SULFUR BALANCE, GRAMS						ADDITIONAL DATA - PERCENT ON DRY BASIS								Sample Moisture (wt%)
		Sulfur In	Sulfur Out			Total Sulfur Out	·S (j)	BTU/LB	Ash	Pyritic S	Sulfate	Organic S	Total S	Nitrogen	Residue Sulfur	
			Coal	Residue	Distillate											
Untreated Coal (5 sample avg) →	3.15± 0.03 (h)	UNTREATED COAL						12,715 ± 130	10.95 ±0.20	1.58 ±0.03	0.05 ±0.03	1.83 ±0.04	3.49± 0.03	1.46		10.1±0.2 (h)
	(i)	TREATED SAMPLES										TREATED SAMPLES				(i)
0-1	3.32	2.94	2.78	0.09	0.01	2.88	-0.06	12,348	11.49	1.56	0.02	1.79	3.37		1.64	1.5±0.2
0-2	3.14	3.08	2.92	0.08	0.02	3.02	-0.06	11,984	10.39	1.44	0.07	1.68	3.19	1.17	1.38	1.5±0.2
0-3	3.02	2.99	2.83	0.07	0.02	2.92	-0.07	11,775	10.28				3.07		1.24	1.5±0.2
0-4	3.42	2.90	2.78	0.09	0.01	2.88	-0.02	12,244	11.35	1.56	0.02	1.89	3.47	1.77	1.58	1.5±0.2
0-5	3.28	3.05	2.97	0.10	0.01	3.08	+0.03	12,342	11.04	1.56	0.01	1.76	3.33	1.96	1.60	1.5±0.2
0-6	3.19	2.71	2.52	0.11	0.01	2.64	-0.07	12,265	11.57				3.24		1.87	1.5±0.2
0-7	3.22	3.06	2.80					12,738	11.14	1.56	0.00	1.71	3.27	1.40		1.5±0.2
0-8	2.95	2.95	2.52	0.10	0.01	2.63	-0.32	12,813	10.90				2.99		1.24	1.5±0.2
0-9	3.04	2.94	2.55	0.19	0.01	2.75	-0.19	12,615	11.55	1.53	0.01	1.55	3.09	1.24	2.12	1.5±0.2
0-10	3.51	2.86	2.75	0.07	0.01	2.83	-0.03	12,378	11.07	1.63	0.04	1.89	3.56	1.74	1.62	1.5±0.2
0-11	3.08	2.90	2.51	0.13	0.01	2.65	-0.25	12,328	11.93	1.41	0.03	1.69	3.13	1.77	1.87	1.5±0.2
0-12	3.33	2.88	2.72	0.13	0.01	2.86	-0.02	12,391	11.48	1.60	0.03	1.75	3.38	1.77	1.94	1.5±0.2
0-13	3.23	2.95	2.72	0.10	0.01	2.83	-0.12	12,492	10.97	1.48	0.30	1.80	3.28		1.38	1.5±0.2
0-14	2.92	2.84	2.34	0.13	0.01	2.48	-0.36	11,516	10.41				2.96		1.72	1.5±0.2
0-15	3.22	2.85	2.69	0.15	0.02	2.86	+0.01	11,598	11.05	1.56	0.11	1.60	3.27	1.24	1.92	1.5±0.2
0-16	3.41	2.83	2.73	0.07	0.01	2.81	-0.02	12,409	11.35	1.59	0.02	1.85	3.46		1.58	1.5±0.2
0-17	3.31	2.92	2.83	0.08	0.01	2.92	0.00	12,356	11.44	1.56	0.01	1.79	3.36	1.97	1.57	1.5±0.2
0-18	3.15	2.83	2.62	0.09	0.01	2.72	-0.11	12,359	10.93				3.20		1.66	1.5±0.2

(h) "As used" samples. (i) Treated and air equilibrated samples. (j) Unaccountable sulfur.

TABLE 34. ORGANIC SULFUR EXTRACTION FROM LOWER KITTANNING COAL ("AS RECEIVED" COAL)

Part 1. Experimental Conditions and Process Mass Balance

Experiment Numbers	EXPERIMENTAL CONDITIONS					MASS BALANCE, GRAMS												
	Solvent	Coal Mesh	Extraction		Filtration Time (Minutes)	Coal Sample In(a)	Dissolved Coal		Treated Coal Dry	Tot-Coal Out(d)	Solvent Retained(e)	Solvent Recovered		Solvent Transfer Losses	Total Solvent Out(g)	Solvent In		Water from Coal	Total "Solvent" In(g)
			Time (Minutes)	Temp. (°C)			Solids(b)	Water(c)				Filtrate Distillate	Drier Trans(f)			Extraction	Rinse		
0-19	p-Cresol	-14	30	180	20	91.[illegible]	0.74	0.9	90.82	92.46	0.96	403.67	23.25	16.72	446.60	360.90	84.3	0.9	446.6
0-20	p-Cresol	-100	30	182	30	97.45	0.73	0.9	97.18	98.81	1.36	433.04	23.85	22.15	480.40	400.20	79.3	0.9	480.4
0-21	p-Cresol	-100	30	166	40	96.74	0.57	0.9	95.21	96.68	-0.06	405.75	24.27	23.94	453.90	383.70	69.3	0.9	453.9
0-22	Nitrobenzene	-14	30	166	20	109.50	0.60	1.0	106.48	108.08	-1.42	407.24	37.65	22.23	465.70	416.80	47.9	1.0	465.7
0-23	Nitrobenzene	-100	30	162	25	99.41	0.52	0.9	98.24	99.66	0.25	426.30	29.56	16.09	472.20	407.30	63.8	0.9	472.2
0-24	Nitrobenzene	-100	30	168	80	103.12	0.65	1.0	101.47	103.12	0.00	393.71	28.56	17.83	440.10	399.90	39.2	1.0	440.1
0-25	p-Cresol	-14	120	186	180	97.07	0.59	0.9	96.38	97.87	0.80	422.77	34.80	23.33	481.70	380.40	100.4	0.9	481.7
0-26	p-Cresol	-100	120	190	60	97.9[illegible]	1.36	0.9	98.62	100.88	2.90	429.18	34.80	25.72	492.60	404.70	87.0	0.9	492.6
0-27	p-Cresol	-100	120	193	60	104.55	1.40	1.0	104.80	107.20	2.61	432.20	27.02	27.23	489.10	400.00	88.1	1.0	489.1
0-28	Nitrobenzene	-14	120	204	[illegible]	102.17	1.27	1.0	98.66	100.93	-1.24	389.80	53.09	32.45	474.10	417.50	55.6	1.0	474.1
0-29	Nitrobenzene	-100	120	210	30	93.81	2.22	0.9	91.60	94.72	0.91	386.10	27.87	21.92	436.80	376.50	59.4	0.9	436.8
0-30	Nitrobenzene	-100	120	198	40	98.00	[illegible]	0.9	95.81	98.12	0.12	406.91	40.43	18.88	466.34	406.14	59.3	0.9	466.3
COAL SAMPLES FROM "SPECIAL" LOWER KITTANNING LOT*																			
0-31	p-Cresol	-14	60	182	30	[illegible]	11.40	1.0	88.2	100.60	5.30	337.80	86.8	25.5	455.40	384.40	70.0	1.0	455.4
0-32	p-Cresol	-100	60	182	20	[illegible]	9.5	1.0	84.8	96.30	-0.70	374.40	80.3	12.0	466.00	331.30	74.0	1.0	466.0
0-33	p-Cresol	-100	60	182	20	95.2	10.0	1.0	86.6	97.60	40	371.00	94.5	23.0	490.90	397.20	92.7	1.0	490.9
0-34	Nitrobenzene	-14	60	182	30	93.5	7.1	0.9	89.6	97.60	2.70	376.20	76.2	20.9	476.00	393.30	81.8	0.9	476.0
0-35	Nitrobenzene	-100	60	188	50	[illegible]	3.0	0.9	87.4	91.30	2.00	291.80	124.4	13.6	431.80	368.40	62.0	0.9	431.8
0-36	Nitrobenzene	-100	60	182	40	[illegible]	4.2	1.0	[illegible]	95.50	-0.70	331.60	120.2	26.2	477.30	390.40	85.9	1.0	477.3

(a) As used (moisture content). (b) Residue recovered from distillation of extraction slurry filtrate. (c) Estimated from water loss of "as used" coal sample dried under conditions identical to the extracted coal conditions (150°C under vacuum). (d) Includes dissolved coal (residue + water). (e) Estimated. This value is subject to the errors in the "dissolved water" weight and it could be higher by the amount of solids lost during operational transfers (0.5 to 1.0 grams normally). (f) Obtained by difference from wet coal (after filtration) and dried coal sample weights. (g) Includes water from coal.

*The "special" lot was a 3-4 kgram sample received prior to the one-half ton received after initiation of this matrix.

TABLE 34. CONTINUED

Part 2. Analytical Data and Sulfur Mass Balance

Exp. No.	Sample Total Sulfur (wt%)	TOTAL SULFUR BALANCE, GRAMS						ADDITIONAL DATA - PERCENT ON DRY BASIS								Sample Moisture (wt%)
		Sulfur In	Sulfur Out			Total Sulfur Out	ΔS(j)	BTU/LB	Ash	Pyritic S	Sulfate	Organic S	Total S	Nitrogen	Residue Sulfur	
			Coal	Residue	Distillate											
						UNTREATED COALS										
Untreated coal (8 sample avg.) →	4.27 ±0.08 (h)							12,299 ±73	19.67 ±0.07	3.62 ±0.03	0.04 ±0.03	0.64 ±0.10	4.31 ±0.08	1.18		0.94 ±0.10 (h)
					TREATED SAMPLES						Treated Samples					
0-19	(i) 4.36	3.91	3.96					12,321	19.45				4.36			(i) Dry
0-20	4.15	4.16	4.03	0.007		4.04	-0.12	12,228	20.03				4.15		0.92	Dry
0-21	4.18	4.13	3.98	0.005		3.99	-0.14	12,221	19.69				4.18		0.96	Dry
0-22	4.35	4.68	4.63	0.008	0.01	4.64	-0.04	12,269	19.71	3.79	0.03	0.53	4.35	1.17	1.31	Dry
0-23	4.20	4.24	4.13	0.008		4.14	-0.10	12,102	19.71	3.63	0.02	0.55	4.20	1.19	1.47	Dry
0-24	4.36	4.40	4.42	0.004		4.42	+0.02	12,109	20.28				4.36		0.68	Dry
0-25	4.24	4.14	4.09	0.005	0.01	4.10	-0.04	12,417	19.00	3.69	0.02	0.53	4.24		0.86	Dry
0-26	4.09	4.18	4.10	0.009		4.11	-0.07	12,287	19.93	3.54	0.02	0.53	4.09		0.63	Dry
0-27	4.19	4.46	4.39	0.009		4.40	-0.06	12,221	19.52				4.19		0.65	Dry
0-28	4.36	4.36	4.30	0.013		4.31	-0.05	12,171	19.79	3.22	0.04	1.10	4.36	1.20	1.01	Dry
0-29	4.54	4.01	4.16	0.021		4.18	+0.17	11,989	20.98				4.54		0.93	Dry
0-30	4.45	4.18	4.26	0.013		4.27	+0.09	12,064	20.76				4.45		0.93	Dry
Untreated coal (3 sample avg.) →	(h) 3.30 ±0.10							11,040 ±70	25.40 ±0.06	2.81 ±0.12	0.05 ±0.02	0.49 ±0.01	3.33 ±0.10	1.15		~1.0 (h)
0-31*	(i) 3.61	3.14	3.18	0.07	0.02	3.27	+0.13	10,347	28.48	3.24		0.40	3.65	1.26	0.65	(i) ~1.0
0-32*	3.57	3.17	3.03	0.06	0.01	3.09	-0.08	10,222	28.93				3.61		0.58	~1.0
0-33*	3.57	3.14	3.09	0.06	0.02	3.17	-0.03	10,324	28.72	3.20		0.40	3.61	1.14	0.58	~1.0
0-34*	3.37	3.13	3.02	0.05	0.02	3.09	-0.04	10,623	26.09	2.89		0.50	3.40	1.31	0.66	~1.0
0-35*	3.08	2.95	2.69	0.02	0.01	2.71	-0.24	10,964	24.74	2.65		0.45	3.11	1.40	0.66	~1.0
0-36*	3.28	3.17	2.96	0.04		3.00	-0.17	10,802	25.89				3.31		0.88	~1.0

(h) "As used" samples. (i) Treated samples (dry). (j) Unaccountable sulfur.

*"Special" lot Lower Kittanning coal.

from the moisture content of the "as received" coal sample (see last column of Part 2) dried under the same conditions as the processed coal (vacuum, 150°C). An assumption was made that extracted coal samples dry to the same extent as untreated coal when subjected to identical drying conditions; therefore, the water from coal remained in the spent solvent fractions (filtrates and traps). This assumption is important in estimating the solvent retained on the coal which was computed as follows:

Solvent Retained = wt. of dry processed coal (Column 10) + wt. solids (Column 8) - wt. of coal sample in

The final 9 columns of Part 1 indicate the solvent mass balance. The "solvent out" value is the sum of the "recovered solvent," solvent losses during operational transfers, and the solvent retained by the treated coal and residue. The "solvent in" quantity is the sum of the weights of solvents used for the extraction and for rinsing the equipment after the extraction as well as the water extracted from coal. It should be noted that processing losses in solvent transfers and vaporization were limited to approximately 5%; coal sample losses were estimated at less than one percent. Thus, process mass balancing was very good.

Part 2 of Tables 33 and 34 presents data on sulfur mass balance and processed coal composition. The first row of the table indicates analytical information on the untreated samples (several sample averages). Each succeeding row furnishes information on the sample treated (extracted) in that particular experiment. The "sample total sulfur" entry refers to the percent total sulfur present in the indicated samples. The value in the first row is the average total sulfur present in untreated coal samples "as used" (wet). This quantity multiplied by the "coal sample in" weight utilized in each experiment furnished the entries of the "sulfur in" column. The percent total sulfur in all other rows is that of the "treated" samples having the moisture content indicated in the last column of the table. The product of each of these percent "total sulfur" values and the corresponding "treated coal (dried)" weight is equal to the "coal sulfur out" entry listed in the second "TOTAL SULFUR BALANCE" column. The column titled "ΔS" represents the difference between total sulfur "in" and "out" - the sulfur that could not be accounted for. The righthand portion of the table lists "additional data" on the composition of untreated (1st row) and treated (processed) coal samples on dry bases, the sulfur content of dry residue (dissolved coal and sulfur), and the moisture content of untreated and treated coal samples determined by vacuum drying at 150°C and air equilibration for 24 hours.

The column headed "Total S" presents values heretofore utilized to compute sulfur removal on the basis of total sulfur content of coal before and after extraction.

The entire bench-scale program on coal desulfurization was performed with samples from a single lot of each of the two coals with the exception of the six experiments presented in the bottom third of Table 34. These data were obtained from a small lot of Lower Kittanning coal available prior to the shipment of the Lower Kittanning coal selected for the program. Comparison of the untreated sample data of the two Lower Kittanning coals indicates that they are quite different, expecially in total sulfur and ash. They also behaved differently during treatment. The "special coal" samples showed higher coal dissolution and solvent retention, but not necessarily higher organic sulfur removal. Experiments 0-31 through 0-36 (special coal samples) were the first performed by the bench-scale personnel. Mass balances are not as good as with later samples, which could be caused by inexperience in handling coal samples; this is most strikingly apparent in the "dissolved coal" column (solids).

Discussion of the data in terms of parametric effects on the process is presented in the next subsection together with the data in Table 35. This table presents data on organic sulfur extractions from pre-dried samples of both coals. The purpose of these 12 experiments was to investigate the combined temperature and moisture effect on organic sulfur removal from the two coals. All coal samples in Table 35 (nominally 100 grams) were dried at about 100°C under 30-inch of mercury vacuum prior to use. One -14 mesh sample and one -100 mesh sample of each coal (Illinois No.5 and Lower Kittanning) were extracted with p-cresol for one hour, filtered, and dried as previously described. A second set of four samples was extracted with nitrobenzene under identical conditions. To a third set, 5% water was added prior to extraction with p-cresol in order to obtain reflux temperatures in the 170°C range (between the extraction temperatures of Tables 33 and 34 and those of dry coal with dry solvent).

Table 35 is divided into four parts. Part 1 lists the important experimental parameters under which the experiments were performed and analytical data on sulfur and moisture analyses. Part 2 indicates the obtained process mass balance during each experiment and the solvent retained by each processed coal sample. Part 3 shows the attained total sulfur mass balances, the organic sulfur composition of untreated and treated (processed)coal samples, and the estimated organic sulfur removal. Part 4 lists composition changes in each processed coal sample (except for total and organic sulfur listed in Parts 1 and 3).

The "Estimated Organic Sulfur Removal" columns list the organic sulfur removal values computed from three sources of analytical data, two of which are totally independent. The first method is based on collected sulfur which consists of sulfur in filtrate residue (dissolved coal) plus sulfur found in filtrate distillate and dryer traps; this sulfur was proven to be organic because sulfur forms analysis of the residue did not indicate the presence of pyrite or sulfates. The second method is based on before-and-after processing total sulfur analysis of each sample (Eschka). The third method is computed from before-and-after processing coal sample analyses for sulfur forms (this is not totally independent from that based on total sulfur, because the organic sulfur content of the coal is obtained by difference between total sulfur and inorganic sulfur - pyrite and sulfate-sulfur determinations).

The values for removal based on total sulfur and sulfur forms are in substantial agreement and indicate up to 50% organic sulfur removals from either coal (see Exps.0-38 and 0-45, Table 34). Since the coal dissolution range is between 4 to 11 wt% for the Illinois No.5 coal samples and 0.5 to 2.5 wt% for the Lower Kittanning samples (10.5% for Exp.0-38 and 1.2% for Exp.0-45), the obtained removals indicate substantial process selectivity toward the extraction of organic sulfur. Also, higher selectivity is indicated for Lower Kittanning coal than Illinois No.5 coal. However, as mentioned above the total sulfur and sulfur forms data sources are not totally independent; therefore, they can not serve as valid cross-checks on accuracy. A true referee method of sulfur removal computation is that based on recovered sulfur. Unfortunately, the values obtained for organic sulfur extraction

TABLE 35. ORGANIC SULFUR EXTRACTIONS FROM DRIED COAL

Part 1. Experimental Conditions and Analytical Data

Exp. No.	Type of Coal	EXPERIMENTAL CONDITIONS: Solvent	Coal Mesh Size	Extraction: Time (Minutes)	Extraction: Temp. (°C)	Filtration Time (Minutes)	ANALYTICAL DATA: Sulfur In "As Used" Sample (% w/w)	Moisture In "As Used" Sample (% w/w)	Sulfur On Dry Basis (% w/w)	Sulfur In Treated Coal (% w/w)	Sulfur In Residue (% w/w)	Sulfur In Distillate (% w/w)	Sulfur In Traps (% w/w)
0-37	Illinois No. 5	p-cresol	-14	60	200	20	3.59 ± .08	0	3.59 ± .08	3.01	1.37	0.02	0.025
0-38	Illinois No. 5	p-cresol	-100	60	202	20		0		2.77	1.50	<0.01	0.025
0-39	Illinois No. 5	Nitrobenzene	-14	60	204	20	← (8 Sample Average)	0		3.39	1.43	0.01	0.01
0-40	Illinois No. 5	Nitrobenzene	-100	60	210	20		0		3.20	1.59	0.15	0.01
0-41	Illinois No. 5	p-cresol	-14	60	177	30		0*		3.07	1.67	0.01	0.01
0-42	Illinois No. 5	p-cresol	-100	60	167	15		0*		3.22	1.32	0.01	0.01
0-43	Lower Kittanning	p-cresol	-14	60	199	20	4.32 ± .10	0	4.32 ± .10	3.33, 3.24	0.36	0.01	0.01
0-44	Lower Kittanning	p-cresol	-100	60	198	15		0		4.43, 4.33	0.43	0.01	0.01
0-45	Lower Kittanning	Nitrobenzene	-14	60	200	25	← (8 Sample Average)	0		4.04	0.70	<0.01	<0.01
0-46	Lower Kittanning	Nitrobenzene	-100	60	210	15		0		3.19	0.61	<0.01	<0.01
0-47	Lower Kittanning	p-cresol	-14	60	170	20		0*		3.90	0.41	0.01	0.01
0-48	Lower Kittanning	p-cresol	-100	60	167	[illegible]		0*		4.39	0.26	0.01	0.01

Part 2. Process Mass Balance

Exp. No.	MASS BALANCE, GRAMS: Coal Sample In (Dry)	Water Added To Coal	Dissolved Coal: Solids[a]	Dissolved Coal: Water	Treated Coal (Dry)	Measured Coal Losses[b]	Total Coal Out	Solvent Retained[c]	Solvent Recovered: Filtrate Distillate	Solvent Recovered: Drier Traps	Solvent Transfer Losses	Total Solvent Out	Solvent In: Extraction	Solvent In: Rinse	Water From Coal	Total Solvent In[d]
Illinois #5 Coal																
0-37	86.8	0	8.7	0	83.1	0.5	92.3	5.8	367.2	83.9	29.8	466.4	336.7	140.7	0	466.4
0-38	73.5	0	7.7	0	71.5	1.0	80.2	6.7		69.1	20.0	420.7	285.4	135.1		420.7
0-39	85.6	0	4.2	0	84.6	0.7	89.5	3.9		[illegible]	32.9	475.2	340.4	134.8	0	475.2
0-40	81.9	0	2.9	0	82.5	0.2	85.6	3.[illegible]		[illegible]	43.2	466.[illegible]	333.3	132.7		466.[illegible]
0-41	87.1	4.5	9.5	4.5	84.7	0.8	99.3	8.3	[illegible]	80.8	36.3	495.0	342.3	148.2	4.5	495.0
0-42	80.0	4.4	6.7	4.4	78.5	0.9	90.5	6.1	360.7	84.7	24.1	475.6	338.8	132.4	4.4	475.6
Lower Kittanning Coal																
0-43	109.6	0	1.9	0	109.4	1.6	112.9	3.3	451.3	33.0	30.3	517.[illegible]	[illegible]	135.5	0	517.9
0-44	97.5	0	1.9	0	93.2	0.5	95.6	-1.97	452.5	33.5	21.67		[illegible]	123.6	0	505.7
0-45	97.5	0	1.2	0	96.7	1.1	99.0	2.5	465.6	45.3	9.6	523.0	393.3	129.7		523.0
0-46	95.4	0	2.3	0	94.2	0.8	97.3	1.9	476.5	29.7	20.3	528.4	382.4	146.0	0	528.4
0-47	93.8	4.9	0.5	4.9	94.4	0.3	100.1	1.4	487.9	28.4	22.7	540.4	391.3	144.2	4.9	540.4
0-48	96.1	5.0	1.2	5.0	97.6	0.6	104.4	3.3	481.7	27.7	29.0	542.5	414.1	123.5	5.0	542.5

NOTES:

a Residue recovered from distillation of extraction slurry filtrate.

b Dry coal on filter papers.

c Estimated from weight gain of solids ("total coal out").

d Includes added water

* Prior to addition of indicated quantity of water.

TABLE 35. CONTINUED

Part 3. Sulfur Mass Balance and Organic Sulfur Removal

EXP. NO.	TOTAL SULFUR BALANCE, GRAMS						ORGANIC SULFUR W/O		ESTIMATED ORGANIC SULFUR REMOVAL (PERCENT)[f]		
	Sulfur In	Sulfur Out				$S_{out}-S_{in}$[e]	Untreated Sample Dry	Treated Sample Dry	Recovered Sulfur	Total Sulfur Before and After Treatment	Sulfur Forms
		Coal	Residue	Distillate	Traps						
Illinois No.5 Coal											
0-37	3.12±.07	2.50	0.12	0.07	0.02	-0.41±.07	1.96±0.17	1.37	12.4 ± 1.0	37 ± 6	33
0-38	2.64±.06	1.98	0.12	0.03	0.02	-0.49±.06	1.96±0.17	1.15	11.8 ± 0.8	46 ± 6	43
0-39	3.07±.07	2.87	0.06	0.03	0.01	-0.10±.07	(8 Sample	1.79	6.0 ± 0.8	12 ± 4	10
0-40	2.94±.07	2.64	0.05	0.05	0.01	-0.20±.07	Average)	1.58	6.2 ± 0.5	17 ± 5	19
0-41	3.13±.07	2.60	0.18	0.03	0.01	-0.32±.07		NA	12.9 ± 1.0	31 ± 6	--
0-42	2.87±.06	2.53	0.09	0.04	0.01	-0.21±.06		NA	8.3 ± 0.6	22 ± 5	--
Lower Kittanning Coal											
0-43	4.73±.11	3.59	0.007	0.04	0.003	-1.09	0.67±0.12	NA	6.8 ± 0.5	100**	--
0-44	4.21±.10	4.08	0.008	0.04	0.003	-0.08	0.67±0.12	NA	7.7 ± 0.5	20 ± 20	
0-45	4.21±.10	3.91	0.008	<0.01	<0.01	-0.29±.10	(8 Sample	NA	1.5	46 ± 20	--
0-46	4.12±.10	3.94	0.014	<0.01	<0.01	-0.17±.10	Average)	NA	1.6	28 ± 20	
0-47	4.03±.09	3.68	0.002	0.05	0.003	-0.35±.09		NA	0	57 ± 20	
0-48	4.15±.10	4.28	0.003	0.05	0.003	+0.13±.10		NA	0	0	

Part 4. Composition Changes im Processed Coals

Exp. No.	ADDITIONAL DATA, WEIGHT PERCENT (DRY BASIS)									
	Heat Content BTU/lb		Ash		Nitrogen		Pyritic Sulfur		Sulfate	
	Before[g]	After[g]	Before	After	Before	After	Before	After	Before	After
Illinois No.5 Coal										
0-37	12,665	12560	11.41	11.68	1.35±.03	NA	1.56±.12	1.64	0.07±.02	0.00
0-38	±75	12501	±0.25	11.34	(8 Sample	1.22	(8 Sample	1.62	(8 Sample	0.00
0-40	(8 Sample	12064	(5 Sample	12.37	Average)	1.90	Average)	1.52	Average)	0.08
0-41	Average)	12160	Average)	11.57		1.85		1.55		0.07
0-42		12512		11.28		NA		NA		NA
0-43		12615		11.23		NA		NA		NA
Lower Kittanning Coal										
0-44	12,292	13264	19.89	14.64	1.16±0.07	NA	3.59±0.17	NA	0.06±0.03	NA
0-45	±98	12049	±0.64	21.10	(8 Sample	NA	(8 Sample	NA	(8 Sample	NA
0-46	(8 Sample	12855	(8 Sample	15.41	Average)	NA	Average)	NA	Average)	NA
0-47	Average)	11708	Average)	22.68		NA		NA		NA
0-39		12303		19.90		NA		NA		NA
0-48		12018		21.03		NA		NA		NA

e Unaccounted sulfur.

f Sulfur removal estimate from three independent groups of data.

g Before and after processing

from this source of data were quite different from those previously quoted. For example, the indicated removal from Exp.0-38 is 11.8 ±0.8% and that from Exp.0-45 is 1.5%. These removal values indicate no apparent process selectivity toward organic sulfur removal. The quantity of recovered sulfur, present principally in the recovered dissolved coal (residue), is proportional to the amount of coal dissolved.

The described discrepancy is present throughout the 48 experiments of Tables 33, 34 and 35. The difference manifests itself best in the $S_{out}-S_{in}$, or ΔS, columns of these tables (Part 2 of Tables 33 and 34, and Part 3 of Table 35). This unaccountable sulfur results from sulfur mass balance computations and represents as much as 80% of the sulfur difference in coal before-and-after processing. The obvious sources of error are:

- Lower than actual total sulfur values in processed coal due to errors in analyses (method defects).
- Lower than actual total sulfur values in residue (same reasons).
- Lower than actual total sulfur values in spent solvent solutions (same reasons).
- Sulfur loss through formation and escape of volatile sulfur compounds during processing.
- Combinations of the above.

If the observed discrepancy is due to the first listed error source, then the second source of error must be present also (same analysis of similar coal matrix subjected to the same solvent). However, the inverse is not necessarily true because of the expected higher volatility of the residue. Thus, from these two sources of error it is concluded that the actual organic sulfur removal value lies between that computed by recovered sulfur and that by before-and-after processing coal analysis; in all probability, closer to that computed by recovered sulfur since a small error on total sulfur analysis of the processed coal translates into a large percent error in computed sulfur removals, while a small error in residue analysis will not affect substantially the quantity of recovered sulfur. Errors due to the third and fourth listed sources will tend to justify the high end of computed organic sulfur removal values (those computed from coal analyses).

Attempts to infer extent of organic sulfur removal from heat content and ash data failed due to the scatter in analytical data. Actually, normal data scatter in these quantities is of the same order of magnitude as expected changes in btu and ash from organic sulfur removals in the 40 to 50% range. Trends were sought but were not indicated.

The sulfur removal discrepancy was discussed at several meetings with experts in the coal analysis area (e.g., U.S. Bureau of Mines Analytical personnel), but no solution was found. All agreed that the identified sources of error are all possible and that others, not identified, may also exist.

Subsequent to analyses of the data from the 48 experiments presented in Tables 33 through 35, literature surveys and discussion with experts failed to reveal the actual source for the observed discrepancy in computed sulfur removal values. Thus, a matrix of special experiments was performed as a check on the analytical methods used. These included:

- Comparison of standard methods for analysis of coals for total sulfur content (Eschka vs Bomb Wash). Duplicate extracted coal samples, including samples from pyritic sulfur extraction experiments, were subjected to both Eschka and Bomb Wash analysis for total sulfur. The results are shown in Table 36.

Table 36. Comparison of Coal Sulfur Analysis Techniques

Sample No.	Bomb Wash %S	Eschka %S
(Pyritic Sulfur Extraction with $FeCl_3$)		
1	2.75	2.86
2	2.77	2.83
(Organic Sulfur Extraction with p-cresol)		
3	3.04, 3.24, 3.20	3.37, 3.36
4	2.73	2.77
5	2.99	3.01

In all but sample 3 the two methods show good agreement. The results from two of the three organic extractions show slightly better agreement between the two methods than the pyritic extractions which had no contact with p-cresol solvent. These results tend to indicate that the total sulfur values for extracted coals are correct. In the case of sample 3, the bomb wash results indicate a larger sulfur decrease than the standard Eschka analysis.

- Dissolved coal residue analysis by three methods. Two one pound samples of Illinois No.5 coal were extracted with p-cresol. The spent solvent from one of the two experiments was carefully distilled to obtain the dissolved coal residue. Approximately 40 grams of dry residue was obtained which was split in four samples. Two approximately 10 gram samples were sent to CT&E for Eschka and bomb wash analysis; the third 10 gram sample was subjected to bomb wash analysis at TRW; the fourth sample was dissolved in 10 times its weight of p-cresol and analyzed by x-ray fluorescence (dissolution was not perfect, some grains of coal remained in suspension). The total sulfur content of the three first samples was 2.2 ±0.2 wt%; the x-ray fluorescence method gave 1.8 wt% sulfur after adjustment for dilution (the solid coal present in the solution rendered the result somewhat uncertain). One half of the spent solution from the second coal sample was distilled to 1/10 of its weight and analyzed by x-ray fluorescence for total sulfur; the other half was distilled to dryness and was analyzed by Eschka. Both samples gave identical results, approximately 2 wt% of sulfur on dry residue basis. These experiments indicated that Eschka analysis of the residue must be correct and the missing sulfur is not in the residue; they also proved that the x-ray fluorescence method for sulfur determinations in solutions containing as low as 0.5 wt% sulfur is as accurate as the Eschka method. Furthermore, the former method was also compared to the lamp combustion method, using very dilute solutions of coal sulfur in p-cresol and nitrobenzene (0.01 wt% sulfur or less); the sulfur analysis results from the two methods were identical.

The above described sulfur analysis investigations proved that the utilized methods are equivalent and probably correct. Thus, it was not possible to identify on the basis of the residue analysis the reason for the observed lack of sulfur mass balance during coal organic sulfur extractions. On the other hand, the obtained process mass balances were too good to justify the observed sulfur imbalance either in terms of coal or solvent losses. It remained to examine the possibility that volatile sulfur compounds escape during processing and are not accounted for, even though laboratory odors did not indicate such occurrence.

A number of experiments were performed to check the possible generation of gaseous sulfur compounds during coal processing. Illinois No.5 extractions with p-cresol were undertaken where the coal leacher, spent solvent distillation unit, and oven-drier were equipped with caustic and zinc solution traps. The results were always negative for sulfur presence. In addition, three special experiments were performed in conjunction with solvent retention determinations (to be described in detail later) which utilized in series room, ice, dry ice and liquid nitrogen traps followed by Ascarite (or Mallcosorb) and Drierite columns. No measurable quantities of volatile sulfur compounds leaving the leacher were detected in these experiments either.

Thus, all attempts to mass balance the sulfur (to reconcile the sulfur removal values determined from recovered sulfur and coal analyses) failed. It is presently believed that when organic solvents such as p-cresol and nitrobenzene are retained by the processed coal in quantities of 3 to 10 wt% (as is the case for the experiments in Tables 33 through 35) analysis of coal for total sulfur becomes inaccurate. This, however, is only speculation based on the facts that volatile sulfur compounds were not found during processing and that the obtained sulfur content of the dissolved coal residue did not account for the missing sulfur. In fact, in order that process organic sulfur selectivity be justified, the residue should have 10 wt% sulfur content for 10 wt% coal dissolution and 50% organic sulfur removal; the assumption can then be made that the removed sulfur resides with the residue.

Until the correct sulfur removal value is identified, conclusions on the efficiency and utility of the sulfur removal process remain uncertain. However, the data obtained on parametric effects, solvent retention and double extractions remains valid since conclusions drawn are based on relative rather than absolute values.

3.3.3.2.1 Effect of Major Parameters on Process Efficiency

Tables 33, 34 and 35 above show that the performed parametric investigations involved:

- Two coals (Illinois No.5 and Lower Kittanning)
- Two sulfur extraction solvents (p-cresol and nitrobenzene)
- Two coal particle top sizes (100 and 14 mesh)
- Extraction time (0.5 to 2 hours)
- Extraction temperature (120°C to 210°C)
- Moisture content of starting coals (0 to approximately 10 wt%)

The data within the described uncertainties indicated the following trends for the effects of the above process parameters on process efficiency:

- Percent organic sulfur removal is approximately the same for either coal, by either method of computation. Selectivity appears to be higher with Lower Kittanning coal than with Illinois No.5 coal from dissolved coal data, but approximately the same from residue composition data. For example, 1 to 2 wt% Lower Kittanning coal dissolution indicates the same removal as 10 wt% for Illinois No.5 coal while their organic sulfur content differs by a factor of 3. On the other hand, residue analysis from the two coals shows a sulfur content approximately equal to the organic sulfur content of the respective coals (see Tables 33 and 34).
- In all cases p-cresol was a more efficient organic sulfur extraction agent than the nitrobenzene.
- In most cases, percent sulfur extraction decreased with increasing coal top size, but the difference was too small for definite conclusions; larger increments in coal top size need to be investigated.
- Extraction time had a substantial effect on organic sulfur extraction rate during the first 60 minutes of leaching, but a diminishing influence between 60 and 120 minutes.
- Extraction temperature appears to be the most influential of all process parameters investigated. The nature of the experiments performed (slurry reflux extractions) tied this parameter to the moisture content of the starting coal. Thus, in precise terms sulfur removal increases with increasing temperature and decreasing moisture content of coal. However, it is believed that the effect of starting coal moisture is restricted to the reduction of slurry reflux temperature. That is, water does not inhibit the extraction by blocking or slowing organic solvent penetration into the coal or by some other mechanism. This deduction was based on the assumption that such inhibiting action would not be moisture concentration dependent within a small range of concentrations (4 to 10 wt% water in coal, or 1 to 2 wt% in slurry). For example, reduction of coal moisture content from 10 wt% to 4 wt% to zero (Illinois coals) increased indicated sulfur removals from 26 to 31 to 46% (from coal analysis), respectively; thus, relatively small changes in slurry water concentrations appear to have resulted in large changes in removal which can not be interpreted in terms of blockage or similar linear type of influence on rate. These large increases in rate can be easily explained, however in terms of the corresponding increases in temperature from 120°C to 170°C. Furthermore, extractions with p-cresol or nitrobenzene, during which water vapor was allowed to escape, refluxed at or near the normal boiling point of the solvent and showed the same organic sulfur removal values as those obtained with dry coal. This indicates that there is no residual coal moisture effect, if any at all. Table 37 gives examples of the above parametric effects on Illinois No.5 coal. It also illustrates that in most cases the indicated trends are discernable regardless of method of of sulfur removal computation, even though removals based on recovered sulfur are too low for precise determinations.

Table 37. Examples of Parametric Effects on Organic Sulfur Extraction from Illinois No.5 Coal

Ref. Exp. No.	Solvent	Coal Top Size	Coal Moist. (wt%)	EXTRACTION		Residue wt% of Init. Coal (Dry)	wt% Organic S Removed computed from	
				Time (Hrs)	Temp (°C)		Coal Anal.	Recovered S
0-37	p-cresol	-14	0	1	200	10	37	12
0-38	p-cresol	-100	0	1	200	10	46	13
0-2 0-3	p-cresol	-100	10	0.5	120	6	10	6
0-8 0-9	p-cresol	-100	10	1.0	120	10	26±2	11±2
0-14 0-15	p-cresol	-100	10	2.0	120	9	34	11±2
0-8 0-9	p-cresol	-100	10	1.0	120	10	26	11±2
0-41	p-cresol	-100	4.5	1.0	170	8	31	12
0-38	p-cresol	-100	0	1.0	200	10	46	12
0-40	Nitrobenzene	-100	0	1.0	210	4	17	6

3.3.3.2.2 Effect of Double Coal Extraction on Organic Sulfur Removal

Two types of double extractions were performed during bench-scale coal desulfurization investigations:

- Double organic solvent extractions, where the coal was leached for one hour, filtered, solvent washed, dried and reprocessed (leached again for one hour, etc.)
- Pyritic sulfur extraction followed by organic solvent extraction (p-cresol), where the coal sample was completely processed by the pyritic sulfur removal process and then extracted with p-cresol for organic sulfur removal.

The first type of double extractions was performed prior to the arrival of the Illinois No.5 and Lower Kittanning coals; thus, the coals used were not those selected for the program. However, two of the three coals tested, Indiana No.V (total sulfur 3.88 wt%, organic sulfur 1.51 wt%) and Bruceton (total sulfur 1.52 wt%, organic sulfur 0.71 wt%) are similar in rank and organic sulfur content to Illinois No.5 and Lower Kittanning coals, respectively. It is believed that conclusions drawn from the investigated coals apply to the latter two coals.

The first one-hour extraction of the Indiana No.V coal (30 mesh top size) resulted in approximately 25 wt% organic sulfur removal. The second one-hour extraction removed only about 5 wt% of the remaining organic sulfur. The ratio of those removals is similar to the equivalent single extraction ratio obtained from -100 mesh Illinois No.5 coal extracted for one and two hours without interruption (see Table 33, Experiments 0-8 and 0-15). It appears, therefore, that the double extraction of the Indiana No.V (and, by extrapolation, the Illinois No.5) coal is equivalent to a single extraction of equal residence time. This is equivalent to concluding that replacing the "spent" solvent after one hour of coal extraction has no effect on the organic sulfur removal at the end of two hours.

The Bruceton coal (30 mesh top size), doubly extracted under the same conditions as the Indiana No.V coal, gave different results. The organic sulfur removal was approximately equal during the first and second extractions. It is not clear whether this implies a constant extraction rate for two hours or indicates experimental uncertainties. The organic sulfur content of this coal is low (0.71 wt%) and the indicated organic sulfur removal of approximately 12 and 15 wt% during the first and second extraction hours, respectively, represent a few milligrams of sulfur; a small error in analysis for total sulfur in processed and unprocessed coal can result in large error in computed sulfur removal. In either case, the indicated organic sulfur removal at the end of two hours was approximately 30 wt% (the same as that for Indiana No.V coal). Thus, it is probably safe to conclude that through the initial two hours of reaction the residence time in the extractor rather than the amount of dissolved sulfur and coal in the solvent is the important factor controlling organic sulfur removal.

The second type of double extraction, organic solvent leaching of virtually depyritized coals, showed that the sequence of sulfur forms leaching is not important to organic sulfur removal. This conclusion was drawn on the basis of the total sulfur content of the obtained dissolved coal residues after extraction of five pyritic sulfur leached Lower Kittanning coal samples with p-cresol. Anomalies in processed coal analysis did not allow conclusions to be drawn on the basis of before-and-after processing coal sulfur content. Details of the double extraction experiments are given below.

Two approximately one pound samples of ferric sulfate leached and completely processed Lower Kittanning coal (Exp.50 and 52, Table 22) were riffled into four samples each. Two of the Experiment 50 (91 wt% of pyrite removed) and three of the Experiment 52 (70 wt% of pyrite removed) samples were extracted in duplicate and triplicate, respectively, with p-cresol at 200°C for one hour and completely processed as described earlier. All five organic extractions yielded a dissolved coal residue containing about one percent of the starting coal weight and all five processed coals exhibited weight gains indicating 1 to 3 percent solvent retention. The obtained coal analyses, on dry basis, are listed in Table 38.

Table 38. Organic Sulfur Extraction Data on Lower Kittanning Coal Treated for Pyritic Sulfur Removal

Exp. No.	Sulfur Analyses (wt%)				Ash (wt%)	Heat Content (Btu/lb)
	Total	Organic	Pyritic	Sulfate		
Starting Coal (Exp.52)	1.91	0.66	1.14	0.11	17.2	12836
0-49	2.56	1.45	0.97	0.13	18.0	12741
0-50	1.99	0.92	0.94	0.14	18.1	13102
0-51	2.15	0.98	1.03	0.14	18.6	12717
Starting Coal (Exp.50)	1.43	0.86	0.32	0.26	16.6	12744
0-52	1.63	1.07	0.32	0.24	17.7	12291
0-53	1.72	1.19	0.27	0.26	17.4	13191
Average change from starting	+0.29	+0.38	-0.11	+0.01	+0.5	+29

These data show a very significant increase in total sulfur (0.3% average) which coupled with a small decrease in pyritic sulfur gives an average 0.4% increase in organic sulfur after extraction. This increase is almost certainly not real and once again it appears that sulfur analysis of a p-cresol treated coal leads to anomalous results. The dissolved coal residues were found to have an average of 1.1% total sulfur. Since the obtained residue weights and sulfur content are similar to those obtained from non-depyritized Lower Kittanning coal extracted with p-cresol (see Tables 34 and 35), it can be concluded that coal leaching for pyrite removal prior to organic sulfur extraction processing has no effect on the efficiency of the latter process.

3.3.3.2.3 Solvent Retention on Processed Coal

The solvent retention on processed Illinois No.5 coal was estimated to be between 6 and 12% the weight of the coal (Tables 33 and 35); since these extractions were performed at 4:1 solvent to coal ratios, between 1.5 and 3.0 wt% of the utilized solvent was retained by the coal. The retained quantities of solvent by the Lower Kittanning coal samples were estimated at 1 to 4% the weight of the coal or up to 1% of the utilized solvent. Preliminary economic analysis of the process indicated that if p-cresol is used as the solvent, retention in excess of one percent the weight of coal would render the process prohibitively expensive. Actually, retention levels of 0.1 to 0.2% of utilized solvent were set as desirable limits. The estimated intolerable levels of solvent retention and the uncertainties associated with the indirect methods of their computation dictated the performance of special experiments designed specifically to accurately determine solvent retention levels.

Three experiments were performed with approximately one-pound samples of Illinois No.5 coal. They were designed to determine a) the solvent retained on a wet starting coal after 24 and 48 hours coal drying time, b) the water extracted from a wet starting coal, and c) the solvent retained on a dry starting coal. These were simulated organic sulfur extractions in that the spent solvent was distilled off the coal without prior filtration; that is, the "extracted" organic sulfur remained on the coal. The coal samples were extracted, solvent and water separated by evaporation, and vacuum dried in a single vessel (reactor) properly trapped for liquid and vapor collection; there were no material transfers during the experiments. Table 39 summarizes the data.

Experiments 0-54 and 0-55 (Table 39) were conducted with one-pound "as received" samples of Illinois No.5 coal (about 10% moisture) and Experiment 0-56 was conducted with a one-pound sample after vacuum oven drying. In each experiment, approximately an equal weight of p-cresol solvent was added to the coal, refluxed for one hour, and removed by distillation into a series of traps. The traps included: room temperature, ice bath, dry ice cooled,

TABLE 39. ORGANIC SOLVENT MASS BALANCES FROM EXTRACTIONS OF WET AND DRY ILLINOIS NO.5 COAL

Part 1. Process Mass Balance

Exp. No.	MASS BALANCE, GRAMS																		Estimated Solvent Retention W/O of	
	Coal Sample IN	Solvent IN	Total Charge	Liquid Collected In				Vapors Collected In		Total Liquid Out	Treated Coal Dry	Total Out	Total Out-In	Net Change In Solids	Net Change In Liquids	Water Collected (From Coal)	Solvent Collected[a]	Net Change In Solvent		
				Receiver	Trap #1	Trap #2	Trap #3	Ascarite	Drierite										Solvent	Coal
0-54	476.43	480.90	957.33	[illegible]	57.96	5.46	0.60	0.48	[illegible]	[illegible]	[illegible]	961.37	+ [illegible]	-50.49	+43.03	54.80	468.4	-11.5	2.6	2.6
0-55	517.90	522.20	1040.10	[illegible]	[illegible]	7.47	1.76	-0.51	2.79	[illegible]	491.90	1042.17	+ [illegible]	-26.10	+26.17	57.42	491.2	-31.0	5.9	6.0
0-56	417.62	505.10	922.72	[illegible]	[illegible]	0.01	0.17	+0.46	[illegible]	436.8	475.21	921.06	+ [illegible]	+ 7.59	[illegible]	[illegible]	491.5	-13.6	2.7	3.3

Part 2. Experimental Conditions and Sulfur Balance

Exp. No.	EXPERIMENTAL CONDITIONS							ADDITIONAL INFORMATION						
	Coal Sample Used	Top Mesh Size	Solvent	Reflux Time Minutes	Reflux Temp °C	Drying Time Hrs	Drying Temp. °C	% w/w H_2O In "As Used" Solvent	% w/w H_2O In Receiver	% w/w H_2O In Traps	Total Sulfur, Grams			
											"As Used" Coal	Treated Coal	Distillate	ΔS
0-54	As Received	100	p-cresol	60	110	48	150	0.34 ± .03	0.32 ± .01	93.3 ± .8	15.57 ± [illegible]	14.61	<0.01	0.96
0-55	As Received	100	p-cresol	60	110	24	140	0.34 ± [illegible]	2.15 ± .15	90.[illegible] ± .2	16.83 ± .41	15.25	<0.01	1.58
0-56	Dried	100	p-cresol	60	200	[illegible]	1	0.34 ± [illegible] (13 Sample Average)	0.26 (Duplicate	91.[illegible] ± [illegible] Analyses)	14.99 ± .33	14.29	<0.01	0.70

[a] Adjusted to "as used" composition

and liquid nitrogen, all vented or evacuated through a tube of Ascarite or Mallcosorb and then through Drierite. After refluxing and distilling, the coal, which still contained the cresol soluble residue, was "dried" of solvent at 150°C under vacuum for 24 or 48 hours, with the emitted vapors led through the same traps. Each fraction was weighed and analyzed. The weight gain for the total system (starting material and equipment) ranged from 0.07 g to 1.67 g for the three experiments (possibly due to minor external moisture pickup on the cold traps). Process mass balance data is shown in Part 1 of Table 39. Column 14, "Total Out-In" indicates excellent mass balance. The "Water Collected" column shows that the 10 ±0.5% moisture of the untreated Illinois No.5 coal, determined by our drying procedure, was completely extracted during the processing, as assumed previously. In fact, an additional 1% of moisture was extracted. However, the solvent retention values are substantially lower than those estimated during previous experiments. This discrepancy is apparently due to drying conditions and the initial moisture content of the coal. In previous experiments, overnight drying was considered adequate for either dry or wet starting coals. In these experiments the minimum drying time was 24 hours. After 24 hours drying, sample 0-56 (dry starting coal) indicated 3 wt% solvent retention (based on either coal or solvent weight since equal amounts were used). Sample 0-55 (wet starting coal) indicated 6 wt% retention; a duplicate coal sample required 48 hours drying time to reach approximately equal solvent retention levels (2.6 wt%) as 0.56 (see Exp.0-54). Thus, it can be concluded that solvent retention depends both on processed coal drying parameters and moisture content of starting coal.

Additional checks on the validity of the solvent retention values indicated in Table 39 were obtained from extracted coal analyses. Table 40 summarizes the pertinent data.

Table 40. Organic Solvent Retention on Illinois No.5 Coal

Experiment No.	0-54	0-55	0-56
Pretreatment	none	none	dried
Reflux temperature (cresol), °C	110	110	200
Drying time	48 hrs	24 hrs	24 hrs
Average drying temperature, °C	150	140	175
Recovered moisture	11.5%	11.0%	1.1%
Solvent retention on coal (±0.5%)	2.6%	6.0%	3.3%
Decrease in coal ash (±2%)	3.4%	6.9%	2.6%
Decrease in coal sulfur (±2%)	7.5%	15.8%	6.7%(a)
Decrease in nitrogen	3.0%	---	---
Decrease in pyritic sulfur	2.6%	---	---
Decrease in organic sulfur	9.5%(b)	---	---

(a) Average of two determinations by the Eschka method which separately gave 6.5% and 6.8% decrease. Two analyses by the bomb wash method gave 10.8% and 18.1% decreases which appear questionable.

(b) Organic sulfur is not independently determined. It is obtained from the difference between total sulfur and pyritic sulfur.

The most complete analysis performed was on sample 0-54. It shows that the 2.6% retained solvent decreased the ash by 3.4%, the nitrogen by 3.0% and the pyritic sulfur by 2.6%. These results are as expected. However, the organic sulfur decreased 9.5% and the total sulfur decreased 7.5%. Experiments 0-55 and 0-56 did not have nitrogen and sulfur forms determined, but both show that the ash decreased in agreement with the retained solvent level. They also show a total sulfur decrease which is 2 to 3 times too large based on solvent dilution of the coal matrix. Because the extraction slurries were not filtered in these experiments and the solvent was vacuum distilled from the reaction vessel, the starting and processed coal composition (on dry basis) should have differed only because of the dilution effect from retained solvent. The abnormal decrease in total sulfur, and as a consequence organic sulfur, illustrates once again the already discussed problem of sulfur imbalance in processes involving the extraction of coals with p-cresol (to a lesser extent nitrobenzene). These experiments appear to indicate that total sulfur analysis is at fault.

3.3.3.3 Process Status

Under normal circumstances, sufficient data in both quantity and quality was generated during the bench-scale organic sulfur process investigations for process economic evaluation and pilot plant design. However, the described uncertainties associated with coal analysis and the stubborn solvent retention problem render pilot plant upgrading of process development premature and detailed process cost analysis futile.

If recovered sulfur values accurately reflect the extent of organic sulfur removal, the process, as defined by the bench-scale investigations, is not effective for selective organic sulfur removal and should either be modified (different solvents, pressurized extraction) or discontinued.

If the obtained values of before-and-after processing total sulfur content of the coal accurately reflect the extent of organic sulfur removal, then the process, as defined, exhibits sufficient promise for further investigation. The new effort should concentrate in reduction of solvent retention values through either modification of utilized drying procedures or through substitution of drying by a solvent displacement unit operation with or without final coal drying. The indicated organic sulfur removals (up to 50%) even if valid, do not necessarily render this organic sulfur removal process desirable as a separate desulfurization scheme unless higher removals are attainable. However, its easy adaptability to the pyritic sulfur removal process would result in a combined coal desulfurization scheme which even at 50% organic sulfur removal levels would be an excellent desulfurization process. That is, a substantially greater number of coal beds throughout the U.S. contain coal which could be processed for complying with federal and local standards of performance for combustion of coal in stationary sources than those beds containing coal which could be rendered acceptable for use by pyritic sulfur removal alone.

3.3.4 Process Design

Current experimental results show that approximately 8% by weight of the feed coal is dissolved during the organic sulfur extraction. If the spent leach solution is then separated from the coal and evaporated, a tar residue is formed which upon further evaporation of solvent becomes coal-like in appearance. Essentially, all of the dissolved coal can be accounted for in the residue, as shown in the previous section.

A conceptual process flow diagram of one possible process design utilizing the approach of organic solvent extraction of coal is shown in Fig.27. P-cresol recycled from the distillation-sulfur compound recovery section (C-1, C-2) is heated to approximately 125°C. The extraction solution is mixed with the pulverized coal in the leacher (T-7) and extracted in a batch mode. The mixture is then filtered (F-8), with the p-cresol (containing dissolved coal) split into two streams, one recycled along with freshly distilled p-cresol, and the other sent to the distillation section for purification. The coal is then dried (D-3) with further recovery of p-cresol and becomes a product of the process unit.

Bench-scale data thus far indicate that light organic sulfur products are not obtained in the organic extraction. Therefore, the light ends distillation (C-1) may not be required. Also, the heavy organic sulfur product compounds become coal-like when dry and separation from the p-cresol by distillation (C-2) would be difficult. The probable separation technique which takes advantage of these two observations is shown in Fig.28. As shown, all or a portion of the sulfur-rich filtrate from the centrifuge is contacted with a hot gas stream in the drying chamber (D-1) causing the solvent to vaporize and the solid residue to pass quickly through the tar phase and form a coal-like particle. The effluent from the drying chamber is passed through a cyclone (C-1) which separates the solid residue particles from the gas stream. The gas stream is then fed to a heat exchanger (E-1) which cools the gas and condenses the solvent from the stream. The condensed solvent is separated from the inert gas stream in surge tank (T-1) and recycled back to the organic sulfur leacher. The inert gas exiting surge tank T-1 is combined with a small make up gas stream, reheated in furnace H-1 and returned to the drying chamber.

3.3.5 Process Cost Estimation

Cost estimates were computed based on the process scheme shown in Figure 27 utilizing the following main operating conditions:

100 tons/hr coal product
5:1 and 3:1 weight ratio of solvent to coal
50% and 100% of the solvent processed after each pass through the leacher

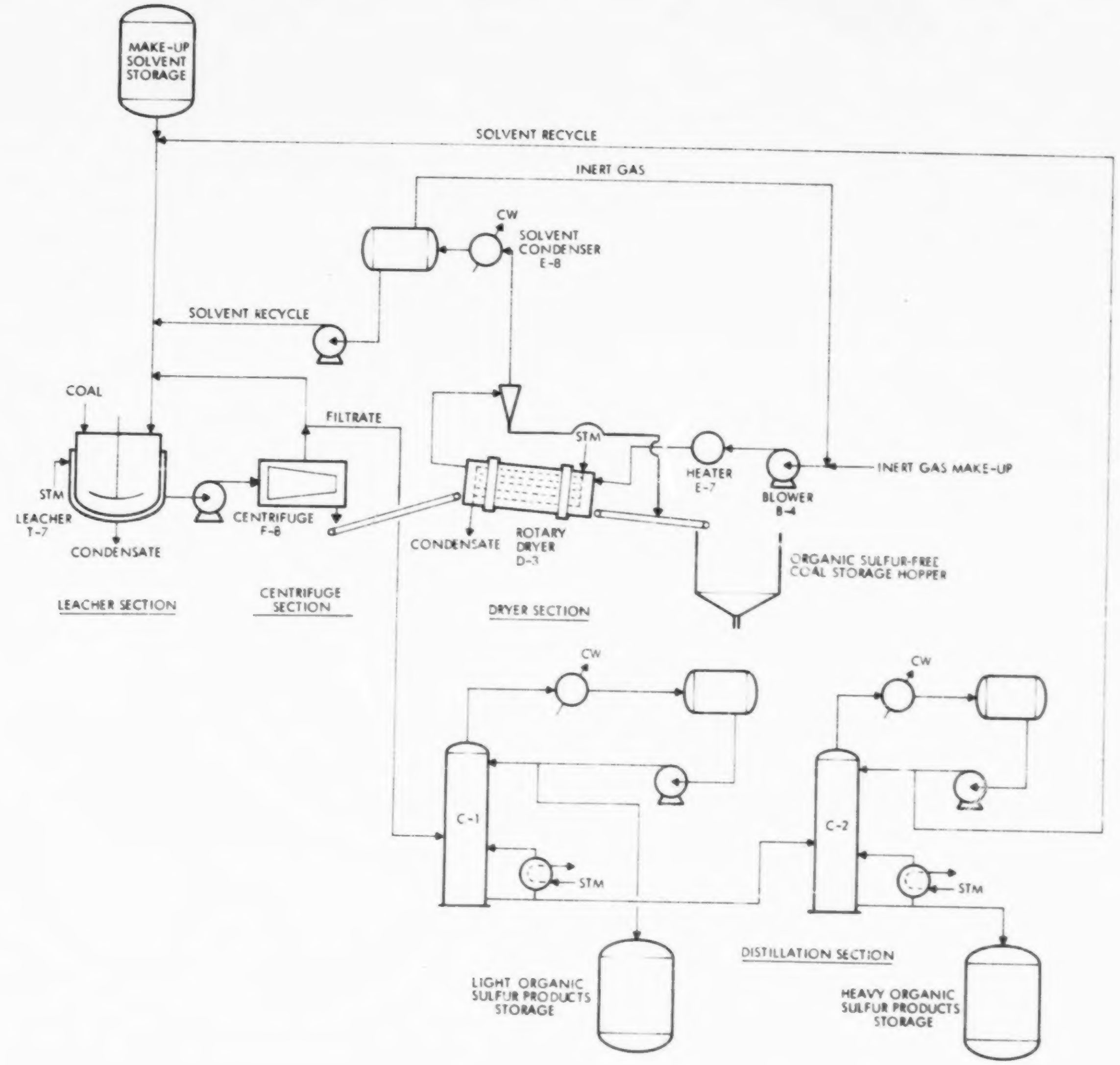

MAKE-UP SOLVENT STORAGE
SOLVENT RECYCLE
INERT GAS
CW
SOLVENT CONDENSER E-8
SOLVENT RECYCLE
COAL
FILTRATE
STM
INERT GAS MAKE-UP
HEATER E-7
BLOWER B-4
STM
LEACHER T-7
CENTRIFUGE F-8
CONDENSATE
CONDENSATE
ROTARY DRYER D-3
ORGANIC SULFUR-FREE COAL STORAGE HOPPER
LEACHER SECTION
CENTRIFUGE SECTION
DRYER SECTION
CW
CW
C-1
C-2
STM
STM
DISTILLATION SECTION
LIGHT ORGANIC SULFUR PRODUCTS STORAGE
HEAVY ORGANIC SULFUR PRODUCTS STORAGE

Figure 27. Organic Sulfur Removal Process Flow Diagram

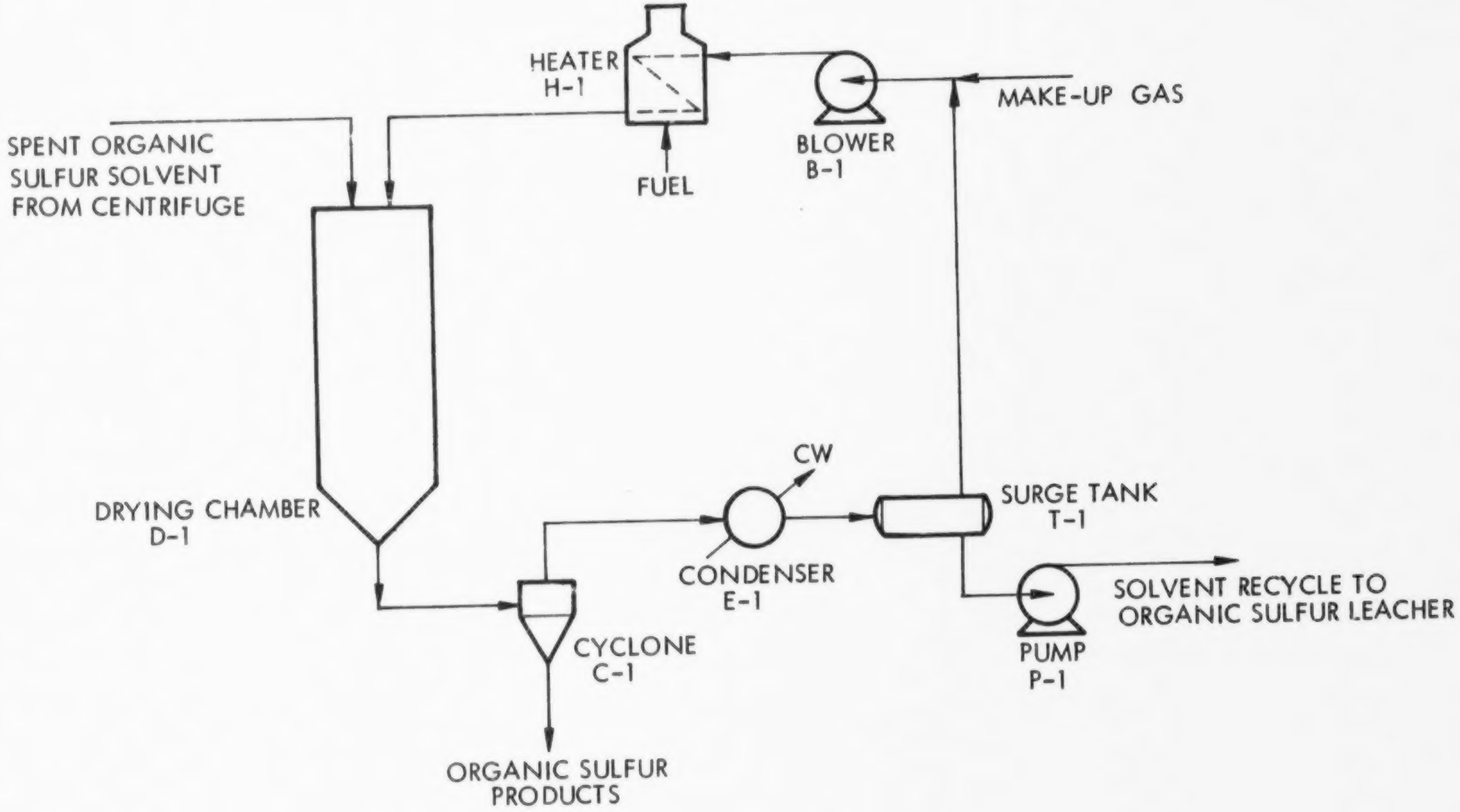

HEATER
H-1
FUEL
BLOWER
B-1
MAKE-UP GAS
SPENT ORGANIC
SULFUR SOLVENT
FROM CENTRIFUGE
DRYING CHAMBER
D-1
CYCLONE
C-1
ORGANIC SULFUR
PRODUCTS
CW
CONDENSER
E-1
SURGE TANK
T-1
PUMP
P-1
SOLVENT RECYCLE TO
ORGANIC SULFUR LEACHER

Figure 28. Organic Sulfur Removal Process Solvent Recovery Section

The results of the economics analysis are given in Table 41, which shows the total capital, operating and labor costs of the current baseline process solvent recovery section ranges from $0.70 to $1.90 per ton of coal. In the solvent recovery process, the major cost-sensitive parameters are the amount of solvent that is processed and solvent losses. If the solvent to coal ratio is 5:1 on a weight basis and all of the solvent is processed after each pass through the extractor, the cost for the solvent recovery section is calculated at $1.90 per ton of coal (with no solvent loss) and the overall cost for organic sulfur removal would be approximately $2.90 per ton of coal. If the solvent to coal ratio is decreased to 3:1, the solvent processing cost is decreased to $2.25 per ton of coal. Finally, if only half the solvent is processed after each pass through the leacher, but the solvent to coal ratio remains at 3:1, the solvent recovery cost and the overall organic sulfur removal costs are estimated at $0.70 and $1.70 per ton of coal, respectively.

Any solvent losses would further increase the operating costs For example, a 0.1% solvent loss w/w coal would add $0.60 per ton of coal (p-cresol) at $.30 per pound to the processing cost. The solvent losses of 5-10% presently found to be absorbed in the coal would be unacceptable from an economic standpoint.

If selectivity of organic sulfur removal is demonstrated, when the analysis ambiguities are resolved, then the processing steps required to reduce the solvent loss will be defined. It would appear that the added steps could include leaching the solvent-rich coal with a less costly, more volatile solvent. Although the conditions are not known, it is likely that this additional processing would add about 50% to the processing cost.

Table 41. Processing Cost Comparison for Organic Sulfur Removal

	Initial Base Case (Solvent Distillation) ¢/ton	Current Baseline Process (Spray Drying) ¢/ton		
Conditions				
• Solvent/Coal, weight ratio	5:1	5:1	3:1	3:1
• Solvent Processing, % per pass	3%	100%	100%	50%
Processing Cost, ¢/Ton				
• Leaching and Separation	20	Same as initial base case		
• Coal Drying	50			
• Solvent Makeup	30			
• Solvent Purification	25	190	125	70
	—	—	—	—
Total Organic Removal Cost, ¢/Ton	125	290(1)	225(1)	170(1)

(1) Does not include the value of coal lost with the sulfur products.

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7.0 GLOSSARY OF ABBREVIATIONS AND SYMBOLS

Abbreviations

Abs	absolute
ASTM	American Society of Testing Materials
btu	British Thermal Unit
cal	calories
eq	equation
Exp.	experiment
Kcal	kilocalories
ml	milliliter
wt	weight

Symbols

A	reaction order with respect to pyrite concentration in coal in leach reactor.
A_L	Arrhenius constant in leach reaction $(\text{hours})^{-1}$ $(\text{wt\% pyrite in coal})^{-1}$.
A_R	Arrhenius constant in regeneration reaction $(\text{minutes})^{-1}$ $(\text{atm})^{-1}$ (liters/mole).
B	reaction order with respect to ferric ion to total iron ratio in leach reactor.
C	concentration.
Δ	difference in quantity following delta.
E_L	activation energy for pyritic sulfur leaching reaction, Kcal/mole.
E_R	activation energy for ferric ion regeneration reaction, Kcal/mole.
K_L	pyritic sulfur leaching rate constant (units same as A_L).
K_R	ferric ion regeneration rate constant (units same as A_R).
μ	micron.
$\underline{M}$	molarity.
mM	millimole.
$\underline{N}$	normality.
P	total pressure, atmospheres.
R	gas constant, cal/mole, °K.

Symbols (cont'd)

r_L	pyritic sulfur leaching rate, weight of pyrite removed per 100 wts of coal per hour.
r_R	ferric ion regeneration rate, moles per liter per minute.
r_S	sulfate to elemental sulfur ratio.
S	sulfur.
S^o	elemental sulfur.
S_o	organic sulfur.
S_p	pyritic sulfur.
S_t	total sulfur.
SO_4	sulfate.
σ	standard deviation.
T	absolute temperature, °K.
t	time, hours (leaching)-minutes (regeneration).
V	volume.
W_p	pyrite concentration in coal, wt%.
Y	ferric ion to total iron ratio.